



# Effects of fermentation residues on the melt processability and thermomechanical degradation of PHBV produced from cheese whey using mixed microbial cultures



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## ARTICLE INFO

### Article history:

Received 15 January 2016

Received in revised form

21 March 2016

Accepted 27 March 2016

Available online 28 March 2016

### Keywords:

Polyhydroxyalkanoate

Mixed microbial cultures

Fermentation residues

Degradation

Melt extrusion

Filament

## ABSTRACT

Two polyhydroxy(butyrate-co-valerate) (PHBV) produced from mixed microbial cultures (MMC) fed with fermented cheese whey (CW) and recovered with different down streaming routes, were processed into filaments by plasticating extrusion. The thermorheological characteristics were improved when fermentation residues were recovered together with the MMC PHBV polymer. Thermogravimetric analysis of the extruded filaments showed that MMC PHBV with 11% residues was less degraded than pure PHBV after the thermomechanical processing. Infrared spectroscopy indicated that residues rich in OH groups were volatilized during extrusion, thereby originating filaments that were less degraded than those produced with purified MMC PHBV. Residues had no impact on the semi crystalline properties of the filaments, but were responsible for their depressed mechanical properties, significant color deterioration upon processing and narrowed the processing operating window of MMC PHBV.

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## 1. Introduction

Among bio-sourced and biodegradable polymers, polyhydroxy(butyrate-co-valerate) (PHBV) is generally accepted as one of the bacterial copolyesters with a brighter future in the plastics industry [1,2]. PHBV is fully compostable as it biodegrades at room temperature under landfill conditions. Its intrinsic biodegradability is best asserted when compared to other bio-based and biodegradable polymers. However, PHBV is not yet a major player in the plastics market, probably due to two main factors. First, PHBV is far more expensive than petroleum-based polymers [3]. Second, PHBV is more challenging to convert into plastic products using conventional processing technologies. Indeed, PHBV shows low viscosity and very little hot melt resistance [4–6]. It also degrades upon melting with a further negative impact on viscosity and final product characteristics. Not surprisingly, thermal degradation of PHBV and other polyhydroxyalkanoates (PHA) has received much

attention, both in terms of the underlying mechanisms [6–16] and how these relate to melt processing (see, for instance [17], and references therein), or in terms of finding routes to improve thermal stability [18–22].

New fermentation routes to accumulate PHA and new down streaming processes to recover PHA could help reducing production costs. The topic has been recently reviewed [3]. PHA produced from mixed microbial cultures (MMC) fed with industrial waste or by-products offer a promising route for a reduction in production costs [23,24], while retaining the physicochemical properties of PHA obtained from the more expensive pure culture systems [25]. PHA recovery and purification also take a strong share of the costs. Purification is needed, as fermentation residues are known to be detrimental to thermal stability [8,9]. However, low amounts (of the order of 2 wt%) of organic fermentation residues were shown to have no impact on the viscoelastic and thermal degradation characteristics of a commercial PHA [11]. Blending unpurified MMC PHBV containing up to 10% fermentation residues with a commercial PHB does not affect the crystallinity, thermal, mechanical and barrier properties of the latter, as long as concentrations of unpurified MMC PHBV remain lower than 10 wt% [26]. In contrast

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to this, larger amounts were claimed to improve the melt viscoelasticity of a biodegradable polymer matrix, whereas the mechanical properties of injection molded specimens were depressed [27]. Therefore, there is a need to clarify what amount and type of fermentation residues can be recovered together with PHA without jeopardizing the rheological properties of the melt, as well as the characteristics of the final product.

For the specific case of MMC PHBV, samples with varying hydroxyvalerate (HV) contents, fermentation residues types and amounts were obtained by the authors from different industrial wastes and recovered using diverse down streaming routes [28]. It was shown that 6 wt% fermentation residues essentially consisting of inorganic matter and water did not affect the crystallinity of the biopolyester, whilst the onset of thermal degradation was significantly lower. The latter was however balanced by a reduced melting temperature and an increased melt viscosity. Similar trends were found when MMC PHBV was recovered with 11 wt% fermentation residues containing up to 5 wt% organic matter. Thus, these results suggested that fermentation residues could actually improve the melt processability of MMC PHBV.

The present work builds on these promising results, addressing the effect of fermentation residues on melt stability and extrudability of MMC PHBV. For this purpose, the production of an unpurified MMC PHBV was scaled up [26,28] to recover an amount of biopolyester sufficient to produce filaments with a prototype mini-extrusion line [29]. The thermorheological characteristics and viscoelastic thermal stability of the MMC PHBV containing 11 wt% fermentation residues are compared with those of a sample submitted to a purification process. The operating window of filament extrusion for these two biopolyesters is compared. Their thermal degradation during melt processing is also investigated by measuring the chemical, thermal and structural properties of the filaments.

## 2. Experimental

### 2.1. Production of MMC PHBV

The MMC PHBV was obtained from the fermentation of an industrial by-product, specifically cheese whey provided by a Portuguese cheese factory (Bel Portugal). A three stage process (reported in detail elsewhere [30–32]) was scaled up [26,28] and is summarized below. In the first stage, organic carbon present in the cheese whey, namely sugars, were biologically converted into precursors for PHA by acidogenic fermentation of the industrial by-product. Then, an efficient PHA-accumulating mixed microbial culture was selected in the second stage. In the third stage, the selected culture was fed with the fermentation products obtained in the first stage, until a maximum MMC PHBV content in the cells was reached. The microbial polyester was then recovered using a down streaming process reported elsewhere [26,28], which included rapid quenching of the microbial activity, followed by degradation of the non-PHA cellular material and, eventually, MMC PHBV centrifugation, washing with distilled water and drying. This MMC PHBV, hereafter labelled as CW89, has been extensively characterized [26,28]. The HV content is 18 mol% and the weight averaged molecular mass is  $1.1 \times 10^5$  g/mol with a polydispersity index of 1.7. CW89 contained 11 wt% impurities, which are characterized as follows:  $3 \pm 1.6$  wt% ash, 0.5 wt% water,  $3.6 \pm 0.3$  wt% proteins and  $0.9 \pm 0.4$  wt% sugars. 50 g of CW89 were purified by dissolving 6 wt% in chloroform at 40 °C during 12 h and at room temperature during 24 h, followed by filtration (0.45  $\mu$ m) and precipitation in 2.5 vol of iced methanol. The precipitate was recovered by filtration, washed with methanol and dried at 60 °C in a vacuum oven overnight. This purified sample, hereafter labelled

CW100, has been previously characterized [28] and revealed the same HV content as CW89. Its weight averaged molecular mass is  $2.5 \times 10^5$  g/mol with a polydispersity index of 1.3. CW100 was obtained without significant fermentation residues, as gas chromatography could not detect any impurity and thermogravimetric analysis indicated that only 1 wt% impurities remained in the sample.

### 2.2. Rheology

CW89 and CW100 powders were compression molded into disks at 150 °C under a 20 tons pressure applied during 3 min. This temperature is well below the onset of thermal degradation (see Figs. 6 and 7) and induces partial melting of the powders (see Fig. 9). The disks allowed fast sample loading into the parallel plates of a stress controlled rotational rheometer (ARG2, TA Instruments) and thus ensured a minimal thermal degradation of MMC PHBV. Disks were loaded at 150 °C, and the temperature was set to 5 °C above the melting point of the powders, whereas the gap was adjusted to 1 mm within roughly 2 min. Exceeding melt was quickly removed from the rim and outer walls of the plates and the samples reached thermal equilibrium within 3 min. Small amplitude oscillatory shear (SAOS) testing was then performed using a strain of 1% and 5% for CW89 and CW100, respectively. These strains were selected from separate experiments carried out to check for the linearity of the stress response, while ensuring the acquisition of a large enough torque. Mechanical spectra were first measured by sweeping the frequency from 100 Hz down to 0.06 Hz. This frequency range allowed the record of a mechanical spectrum within a much shorter time than the kinetics of the thermal degradation of the samples. This frequency sweep was repeated every 10 min over 1 h, as to probe the time evolution of the rheological parameters, namely the storage modulus  $G'$  and the loss modulus  $G''$ .

### 2.3. Extrusion of the filaments

The miniature extrusion line used to process CW89 and CW100 powders into filaments has been described in detail elsewhere [29]. This prototype set-up was designed to mimic the thermo-mechanical stresses developed in larger scale plasticating extruders. The single screw extruder (the 3-zone screw has an external diameter of 6 mm and a length to diameter ratio of 11.5 and contains a barrier-mixing zone) was coupled to a capillary die of 1 mm diameter. For screw speeds in the range 20–60 rpm, throughputs vary typically between 8 and 20 g/hour. Thus, few grams of powder materials were converted into filaments that were cooled at room temperature without applying any drawing. Screw speed and barrel/die temperature were varied to screen the processability of CW89 and CW100.

### 2.4. Characterization of the filaments

The mechanical properties of selected filaments were characterized by flexural testing using an INSTRON 4505 universal testing machine. Tensile testing could not be carried out, as the cylindrical filaments slipped at the grips of the machine. 3 cm long and straight (no bending) samples were cut from filaments showing no surface defects and uniform radius. The thermal stability of the filaments was assessed by thermogravimetry (TGA) using a TA Q500 (TA Instruments). The temperature was swept from 30 °C to 600 °C at a heating rate of 20 °C/min under air atmosphere. Typically 10–20 mg samples were used. Similarly, TGA was performed on CW100 and CW89 powders dried overnight at 60 °C. Differential scanning calorimetry (DSC) was carried out on 4–8 mg filament

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