

COMPARISON OF THE PROPERTIES OF BIOGENIC WINE BY-PRODUCTS STABILIZED BIOCOMPOSITES COMPOUNDED WITH A MINIATURIZED SINGLE-SCREW EXTRUDER AND A CO-ROTATING TWIN-SCREW EXTRUDER

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ABSTRACT

Bioplastics research is hindered by high material prices and limited availability of biopolymers. For conventional compounding, even on lab-scale, large quantities of material are required. In this study, an alternative process for compounding biocomposites was evaluated to investigate the potential of wine-derived biogenic by-products as functional fillers. Formulations based on poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and wine grape pomace (WP) with filler contents up to 10 wt.-% were prepared. The materials were processed with a modified miniaturized single-screw extruder (MSE) and compared to a lab-scale twin-screw extruder (TSE). Thermal and rheological properties of the materials were determined using GPC, MFR, DSC, TGA and OIT. The mixing quality of both extruders was evaluated by optical microscopy imaging. The results revealed that the MSE represents an efficient alternative for research purposes, but differences in the dominant degradation mechanisms during processing must be considered. Thermal analysis showed that WP successfully suppressed the thermo-oxidative degradation of PHBV.

1. INTRODUCTION

The shift towards sustainable materials is inevitable and is a high-priority focus in the plastics industry. Research and development in recent years led to sustainable alternatives for fossil-based polymers such as polyolefins. Although their counterparts based on renewable resources show comparable mechanical properties and are feasible for conventional polymer processing techniques, biopolymers such as biopolyesters require further improvement to access broad applications. Research plays a key role in the process of catching up with decades of development of conventional plastic materials. Unfortunately, current high material prices and limited availability of biopolymers present challenges in research efforts focusing on improving their material properties and extending their fields of applications.

A state-of-the-art process for compounding polymer blends and composites is the use of a twin-screw extruder (TSE). This technique is well established, but even on lab-scale, large quantities of materials are required, e.g., due to process setup and scrap during production. The associated costs limit the overall progress of bioplastics research. Less material-intensive processes such as hot-pressing of pre-mixed materials are often used for preliminary investigations. However, such non-industrial or non-continuous processes are not comparable to methods used in final



applications. One approach to overcoming these hurdles is to miniaturize standard processes while maintaining their main characteristics. For this purpose, miniaturized single-screw extruders (MSE) show great potential to be used as small-size compounders for smallest quantities at increased material efficiency. Here, the term “miniaturized” is used to describe desktop machines which, despite downscaling, have identical features (e.g., L/D-ratio) and comparable properties to industrial extruders. MSEs are mainly designed for 3D printing filament extrusion. Recently, MSEs equipped with a 3-zone-screw with additional mixing elements at the end of the screw have been developed to improve mixing quality. Thus, MSEs can be used for compounding additives into a polymer matrix. This use-case is particularly attractive for research on rare and/or expensive materials such as biopolyesters and alternative additives. The process design is simple, equipment is minimal, and less material is required. Previous studies successfully used MSEs for the extrusion of composite 3D printing filaments filled with inorganic and organic fillers [1–3]. However, these investigations did not compare the MSE processing with conventional compounding processes using a co-rotating TSE. Polyhydroxyalkanoates (PHAs) such as poly(3-hydroxybutyrate) (PHB) and its copolymers such as poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) are promising biopolyesters produced by fermentation polymerization of biomass. Despite having properties comparable to conventional petroleum-based mass polymers such as polyolefins, PHAs are highly susceptible to degradation. During a single step processing, by compounding or extrusion, the molecular weight of the polymer is strongly reduced by up to 50% due to thermal, mechanical, and thermo-oxidative degradation mechanisms [4]. Commercially available PHBV grades are mostly stabilized by adding conventional synthetic antioxidants, which negatively affect the sustainability of these materials. To create fully bio-based and sustainable materials, the stabilizers must be biogenic and correspondingly based on renewable materials. Potentially suitable biogenic materials include wine grape pomace (WP). Consisting of grape seeds, stems, and skins, this substantial unused, low-value winemaking by-product provides high contents of functional substances such as polyphenols [5]. These natural antioxidants may act as stabilizers for biopolymers. Previous studies have demonstrated a great potential for use of WP as bio-fillers to modify the properties of biopolyesters [5–7].

The aim of this research is to evaluate a new, material-saving, industry-oriented process for compounding biocomposites to investigate the potential of WP as a functional bio-filler to improve the stability of biopolyesters. A schematic overview of the study divided into the preliminary works, the biocomposites processing, and the investigations of the influence of the extruder type and the bio-filler is shown in Figure 1.

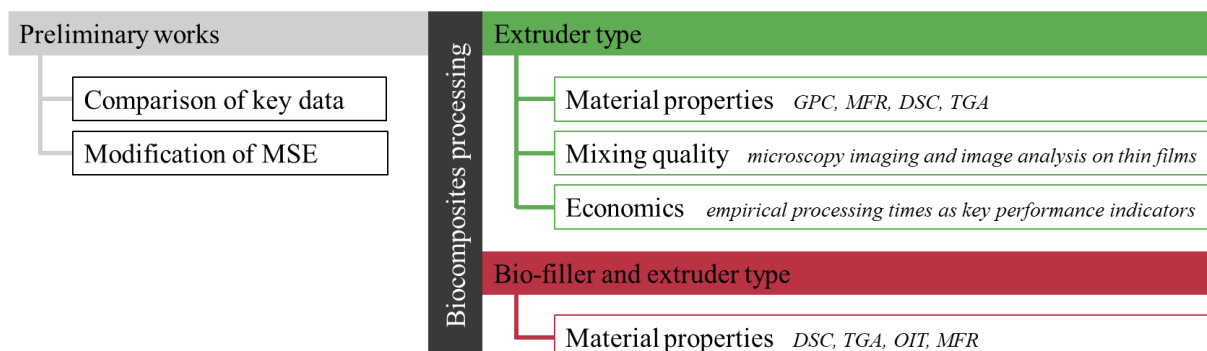


Figure 1: Schematic overview of the present study

The properties of the processed materials, the mixing quality, and the economics are evaluated for the comparison of the extruder types. For this approach, an MSE intended for filament production is compared to a co-rotating TSE used in standard processes. Biocomposites based

on PHBV were chosen as the material system for comparison. Micronized WP was used as a sustainable filler. By establishing such a material-saving, alternative process, the progress of sustainable material research will be accelerated.

2. MATERIALS AND METHODS

In this research, neat and filled PHBV grades were processed with a Composer 450 MSE equipped with a mixing screw (3D Evo B.V., NL) as well as a lab-scale co-rotating TSE type LTE20-44 (Labtech Engineering Co., Ltd, Thailand). Both extruders are characterized by screw diameters of 20 mm and a L/D-ratio of 15:1 for the MSE and 44:1 for the lab-scale TSE. The processing parameters and the final properties of the processed materials were used to compare the performance of both extruders. Biocomposites based on PHBV powder Enmat™ Y1000 (TianAn Biologic Materials Co., Ltd., CN) and WP were prepared and characterized. WP from *Vitis vinifera* subsp. *vinifera* of the red grape variety *Domina* (RWP-Dom) was kindly provided by the winery Richard Dahms GmbH (Schweinfurt, DE) during harvesting in October 2021. The fresh WP was simultaneously dried and grinded to a fine powder with a TurboRotor mill at Mahltechnik Görgens GmbH (Dormagen, DE). The resulting bio-filler powder had a mean particle size of 16.80 µm and a relative moisture content of 2.76%, as reported in a previous study [5]. Various filler contents of the by-product (0, 1, 2, 3, 5, and 10 wt.-%) were pre-mixed and processed with the MSE. Temperatures of 25, 85, 185, and 175 °C from feeder to nozzle and a screw speed of 15 rpm were used. The automatically adjusted filament diameter was set at 1.75 mm and a fan power of 65% was used for forced air cooling of the extrudate. To compare the extruder types, filler contents of 0, 3, 5, and 10 wt.-% of RWP-Dom were additionally processed with the TSE. For the TSE, a screw configuration for filler incorporation via side feeding was used. It consisted of a kneading zone and a first degassing after melting the matrix material. Subsequently, the filler was introduced via side feeding followed by a main mixing and second degassing zone. A second mixing zone was used for dispersive mixing closely to the die, as reported in [5]. The temperature profile was 140-145-150-155-160-160-160-160-165-165 °C from the feeder to the die. The screw speed was set to 230 rpm and a gravimetric dosing system (Scholz Dosiertchnik GmbH, Großostheim, DE) was used for a material throughput of 1.5 kg/h. The extrudate was cooled in a water bath and then granulated. For both MSE and TSE processing, the PHBV powder was dried for 2 h at 60 °C in a dry-air T 5050 E laboratory oven (Heraeus Noblelight GmbH, Hanau, DE).

The results obtained could not only be used to determine the mixing quality of the different processes but also to investigate the stabilizing effects of the biogenic wine by-product. Thermal and rheological properties were determined using standard polymer analyzing techniques: gel permeation chromatography (GPC), melt flow rate analysis (MFR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and oxidation induction temperature analysis (OIT). GPC was performed by Fraunhofer LBF (Darmstadt, DE) using an Agilent SEC 1100 (Agilent Technologies, Inc., Santa Clara, CA, US) and hexafluoro-isopropanol (HFIP) as an eluent to determine the average number-molecular weight (M_n), the average weight-molecular weight (M_w), and the polydispersity index ($\mathfrak{D} = M_w/M_n$). To quantify the process-related degradation, a degradation parameter K was calculated according to Equations (1) and (2), where the values indexed as "unprocessed" present the virgin and the values with the index "processed" present the neat material molecular weights [8].

$$K_{Mn} = \frac{Mn_{unprocessed}}{Mn_{processed}} \quad (1)$$

$$K_{Mw} = \frac{Mw_{unprocessed}}{Mw_{processed}} \quad (2)$$

MFR was determined with a MeltFloW@on from Emmeram Karg Industrietechnik (Krailling, DE) at 180 °C and 2.16 kg. For thermal analysis a Netzsch DSC Polyma 214 System was used (NETZSCH-Gerätebau GmbH, Selb, DE). Sample masses of 15.0 ± 1.0 mg were heated from -40 to 200 °C at a rate of 20 K/min in a nitrogen atmosphere. Two heating scans separated by one cooling scan were performed to obtain the melting peak temperatures (T_m) and the melting enthalpies (ΔH_m) from the heating scans, and the crystallization peak temperature (T_c) from the cooling scan. Due to the comparatively low 3HV content of about 2 wt.-%, the degree of crystallinity (X_c) was calculated according to Equation (3) using $\Delta H_m^0 = 146.6$ J/g of 100% crystalline PHB [7].

$$X_c \% = \frac{\Delta H_m}{\Delta H_m^0(1-w)} \times 100 \quad (3)$$

Dynamic OIT measurements were conducted with the same device using 5.0 ± 0.5 mg of the samples and oxygen as a purging gas. The samples were heated from 25 to 350 °C in an open aluminum crucible at a heating rate of 20 K/min. The degradation temperatures (OIT_{off}) as indicators for the thermo-oxidative stability of the compounds were determined using the offset method with a Δ of 0.05 W/g. A Netzsch TG 209 F3 Tarsus was used for TGA. A sample mass of 9.5 ± 0.5 mg was heated from 40 to 600 °C at a constant heating rate of 10 K/min. The measurements were performed in a nitrogen atmosphere to obtain the temperature at a mass loss of 10% ($T_{10\%}$). The onset temperature (T_{on}) was determined using a tangential approach at the peak temperature (T_p) obtained from the derivative mass loss curve (DTG).

To evaluate the mixing quality of the different processes, microscopic investigations were performed on hot-pressed 30 μ m thin films of the biocomposites. A hydraulic laboratory press P 200 S by Vogt (VOGT Labormaschinen GmbH, Berlin, DE) was used to hot-press a single granule at 180 °C with a system pressure of 15 bar for 1 min, followed by 50 s with 20 bar, and a final step using 1 min with 25 bar. Distributive and dispersive mixing were evaluated by image analysis using ImageJ (NIH, US) software on images taken with an optical microscope VHX 950F (Keyence Deutschland GmbH, Neu-Isenburg, DE). The Morisita's index (I_δ), the skewness (β), the coefficient of variation (v) for the mixing quality, and the degree of disaggregation (k) were calculated using the Equations (4–7) to evaluate the distributive and dispersive mixing efficiency of the extruders:

$$I_\delta = \frac{1}{n} \cdot \sum_i^n \frac{N_i \cdot (N_i - 1)}{N_{total} \cdot (N_{total} - 1)} \quad (4)$$

Where n represents the number of image sections, N_i represents the number of particles per image section, and N_{total} represents the total number of particles [9];

$$\beta = \frac{n}{(n-1)(n-2)} \cdot \sum_i^n \left(\frac{N_i - N_{mean}}{\sigma} \right)^3 \quad (5)$$

Where N_{mean} represents the mean number of particles per image section, and σ represents the standard deviation of the N distributions [9];

$$v = \frac{\sigma_c}{\bar{c}} \quad \text{with} \quad \sigma_c = \sqrt{\frac{1}{n-1} \cdot \sum_i^n (c_i - \bar{c})^2} \quad \text{with} \quad c = \frac{A_{particles}}{A_{total}} \quad (6)$$

Where σ_c represents the standard deviation, c_i represents the concentration in section i , \bar{c} represents the empirical mean concentration, $A_{particles}$ represents the cumulative area of the particles per image section (μm^2), and A_{total} represents the total area of the image section (μm^2) [10];

$$k = \frac{d_0}{\bar{d}} \quad (7)$$

Where d_0 represents the mean particle size before processing (μm) and \bar{d} represents the mean particle size after processing (μm) [11], assuming that the particles have circular areas, which was confirmed by microscopic images. For each composite material five thin films were investigated using four adjacent images (= 20 sections in total) at a magnification of X200. The machine set-up times, the material throughput, and the material losses during process start-up and material changeovers were tracked to compare the economics of the two extruders.

3. KEY DATA COMPARISON OF THE EXTRUDER TYPES

First, the potential of the MSE for use as material-saving, miniaturized compounder was evaluated by comparing the technical data and the qualitative performance indicators based on the experience from experimental applications with those of a conventional lab-scale TSE. The corresponding data for the extruders used in this study is reported in Table 1.

Table 1: Comparison of technical data and qualitative performance indicators of the extruder types

Parameter	Unit	MSE	TSE
Screw configuration	(-)	3-zone-screw with mixing elements	modular screw configuration
Number of screws	(-)	1	2
Screw length	(mm)	300	880
Screw diameter	(mm)	20	20
L/D ratio	(-)	15:1	44:1
Machine height / length / width	(m)	0.5 / 0.5 / 0.3	2.0 / 6.0 / 1.0
Number of heating zones	(-)	4	11
Filler introduction	(-)	Main feeder	Main / side feeder
Dosing	(-)	Pre-mixing	Gravimetric dosing
Max. screw speed	(rpm)	15	800
Max. processing temperature	(°C)	450	400
Min. required material quantity	(kg)	0.1	1.0
Residence time	(s)	250 (at 15 rpm)	44 (at 230 rpm, 1.5 kg/h)
Degassing zones	(-)	0	2
Infeed cooling	(-)	By modification	Standard
Extrudate cooling	(-)	Forced air	Water bath / air
Extrudate cooling efficiency	(-)	Low	High
Shear forces / mechanical stress	(-)	Low	High
Usability	(-)	Rather simple	Rather complex

Due to the different design of the extruders, fundamental differences regarding the machine configuration are obvious. While the TSE has a higher L/D ratio and offers the possibility of a modular screw design, the MSE shows benefits by being smaller in size, requiring less space in the lab. On the other hand, the MSE offers fewer setting options with only four heating zones and a substantially lower maximum screw speed. Additionally, pre-mixing of the materials is required, and feeding is limited to the main feeding option for the MSE. Since aliphatic biopolyesters such as PHAs are susceptible to thermal degradation and hydrolysis [4,8], the

substantially longer residence time and missing degassing options may cause degradation when processing such materials with the MSE. Another significant difference in the processing design is in the cooling of the extrudates. With the water bath of the TSE, higher cooling rates can be applied when compared to the forced air cooling of the MSE. Concerning qualitative performance indicators, based on experiences from previous experiments, the extrudate cooling efficiency and the shear forces applied are lower for the MSE [10,12], whereas its usability is rather simple compared to the TSE. However, some negative aspects of the MSE design, such as the lack of an infeed cooling, can be fixed by modifying the MSE as described in section 4.

4. MODIFICATION OF THE MINIATURIZED SINGLE-SCREW EXTRUDER

After initial trials, the MSE was modified to enable stable processing of the PHBV powder. A schematic illustration of the modifications is shown in Figure 2. To avoid premature melting of the PHBV, the feeding zone was separated from the heating zones with an additional, insulated separator plate. Fans for air intake and outlet were installed for cooling in the separated feeding zone. A 3D printed sealing was installed to avoid airflow in the hopper caused by the forced air cooling. The original fiberglass wool insulation of the extruder heating units was substituted by an improved fiberglass insulation fabric laminated with aluminum. These modifications reduced the temperature in the feeding zone from 120 to 75 °C to achieve sufficient material conveying. To ensure a constant feeding of the powder material, a vibrating feeder unit was installed, equipped with an additional wiper to prevent material bridging.

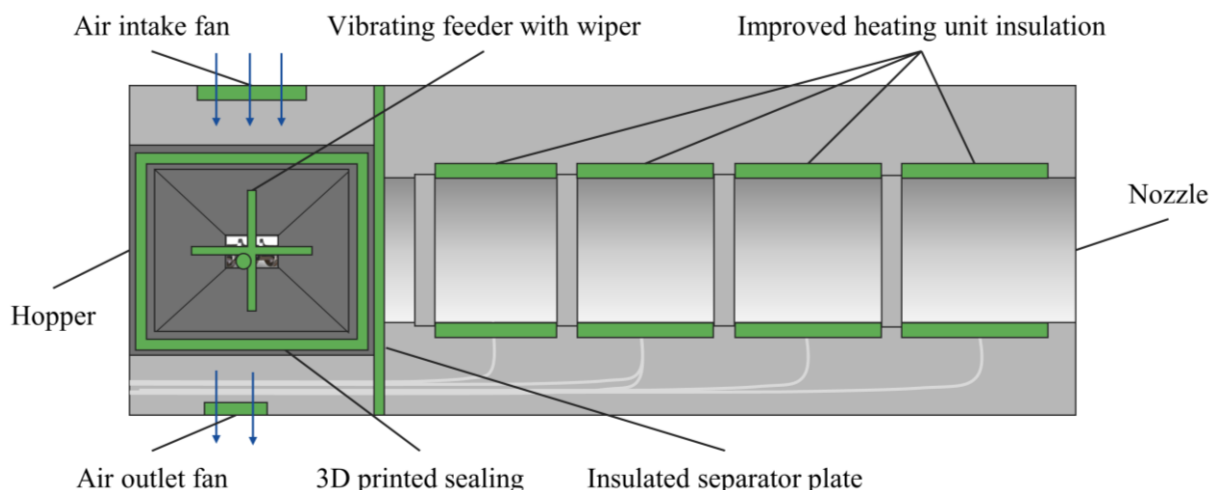


Figure 2: Schematic illustration of the modifications applied to the MSE

5. RESULTS AND DISCUSSION

5.1 Influence of the extruder type on the properties of neat PHBV

Neat materials and virgin PHBV powder were investigated to evaluate the influence of the extruder type on the properties of non-filled material. The data obtained from GPC analysis and MFR measurements are reported in Table 2. The melt-processing with both extruder types led to remarkable reductions in the molecular weights of PHBV compared to the virgin powder material. The molecular weights M_n and M_w were reduced by 41% and 20% through processing with the MSE, and by about 68% and 30% using the TSE, respectively. Accordingly, the degradation parameters K were higher for neat PHBV processed with the TSE, indicating a stronger cleavage of the macromolecular chains into shorter fractions. The molecular weight distribution was broadened as shown by the increased Đ (+120% for neat TSE) [8]. The Đ of

neat MSE was closer to the value of the virgin PHBV, which can be explained by thermal degradation based on cis-elimination and random chain scission reactions being the dominant degradation mechanism during processing using the MSE [4,8]. The process-induced changes in the molecular weights of the neat PHBV resulted in increased MFR-values [4]. Although, according to the literature, thermal degradation through random chain scission reactions is reported as the main degradation mechanism of PHAs [4,7], the thermomechanical degradation caused by higher shear rates during processing with the TSE appeared more crucial [10]. Even though the residence time for the MSE is almost six times longer (Table 1), leading to increased thermal stresses, the thermomechanical stresses applied in the TSE process resulted in stronger molecular weight reductions.

Table 2: GPC and MFR data of virgin and neat PHBV

Sample	M_n (kg/mol)	M_w (kg/mol)	\bar{D} (-)	K_{Mn} (-)	K_{Mw} (-)	MFR (g/10 min)
Virgin	165.91	504.84	3.04	-	-	3.678 ± 0.315
Neat MSE	97.45	402.65	4.10	1.25	1.70	4.297 ± 0.342
Neat TSE	52.84	352.05	6.70	1.43	3.14	5.064 ± 0.356

The thermal properties of neat and filled PHBV processed with both extruder types are reported in Table 3. The degree of crystallinity X_c of the materials, obtained from the first DSC heating scan, shows the influence of the process [13]. Materials processed with the MSE showed a slightly higher X_c compared to the TSE. The difference of 5% for the neat PHBV can be ascribed to the forced air cooling of the MSE with lower cooling rates compared to the water bath cooling of the TSE [13]. Accordingly, T_c of the MSE processed material was about 10 K higher. However, the melting peak temperature T_m and the degree of crystallinity X_c obtained from the second heating scan remained almost constant regardless of the extruder type.

Table 3: DSC data of neat and RWP-Dom filled PHBV

Filler Content (wt.-%)	ΔH_m^1 (J/g)	X_c^1 (%)	T_c^2 (°C)	T_m^3 (°C)	ΔH_m^3 (J/g)	X_c^3 (%)
MSE						
0	90.55	62	73.1	174.3	89.40	61
1	87.55	60	75.8	174.2	91.02	63
2	88.74	62	80.0	174.5	90.92	63
3	84.19	59	77.3	174.9	89.12	63
5	87.77	63	76.6	173.9	88.22	63
10	81.46	62	76.7	174.9	82.49	63
TSE						
0	83.78	57	62.9	174.3	91.83	63
3	82.40	58	75.4	173.2	89.50	63
5	74.72	54	74.7	173.9	88.33	63
10	81.56	62	75.6	173.3	84.56	64

¹ obtained from the first heating scan; ² obtained from the cooling scan; ³ obtained from the second heating scan.

Thermal analysis by TGA revealed reduced thermal stability for materials processed using the MSE as reported in Table 4. The degradation temperatures for the MSE processed PHBV neat were 13.4–15.9 K lower compared to the TSE processed material. Accordingly, the dominant degradation mechanisms during processing varied between the different extruder types: higher shear rates in the TSE resulted in increased mechanical degradation of the material as seen by GPC and MFR analysis, whereas higher thermal stress was applied to the material in the MSE due to longer residence times.

Table 4: Thermal and thermo-oxidative stability of neat and RWP-Dom filled PHBV

Filler Content (wt.-%)	$T_{10\%}^4$ (°C)	T_{on}^4 (°C)	T_p^4 (°C)	OIT_{off}^5 (°C)
MSE				
0	263.1	269.1	280.7	241.8
1	275.1	276.9	287.4	251.7
2	274.6	275.8	284.0	255.9
3	271.3	272.6	279.9	- *
5	259.4	260.8	268.3	- *
10	252.8	252.3	260.2	- *
TSE				
0	279.0	282.7	294.1	239.7
3	271.3	272.8	280.6	- *
5	265.4	266.9	271.5	- *
10	248.5	248.6	256.7	- *

⁴ determined by TGA; ⁵ determined by dynamic OIT; * exothermic effects were completely suppressed.

5.2 Influence of the extruder type and the bio-filler on the properties of PHBV

As reported in Table 3, the main thermal characteristics of the PHBV regarding T_m and X_c , obtained from the second heating scan, were maintained up to filler contents of 10 wt.-%. While at lower filler contents the extruder types led to differences in the characteristics obtained from the first heating scan, the addition of 10 wt.-% RWP-Dom led to almost identical values for both extruder types. This indicates that the influence of the bio-filler might have been stronger than the extruder type. As previously reported by Hiller et al. [5], the WP-filler did not substantially affect the degree of crystallinity of the biocomposites. However, T_c was slightly increased, indicating mild nucleating effects of the bio-filler [13].

By incorporating the biogenic by-products, the thermal degradation, determined by TGA, occurred at lower temperatures for the TSE but showed a mild increase for the MSE, as reported in Table 4. The lower intrinsic thermal stability of the by-products compared to the matrix polymer led to an overall reduced thermal stability with increasing filler content [5–7]. Accordingly, the WP-filler did not act as a pronounced thermal stabilizer, but partly reduced the negative impact of the MSE at low filler contents.

The OIT measurements revealed thermo-oxidative stabilization effects. The thermo-oxidative stabilization is shown in Figure 3 comparing the OIT graphs of neat and filled PHBV processed with the MSE.

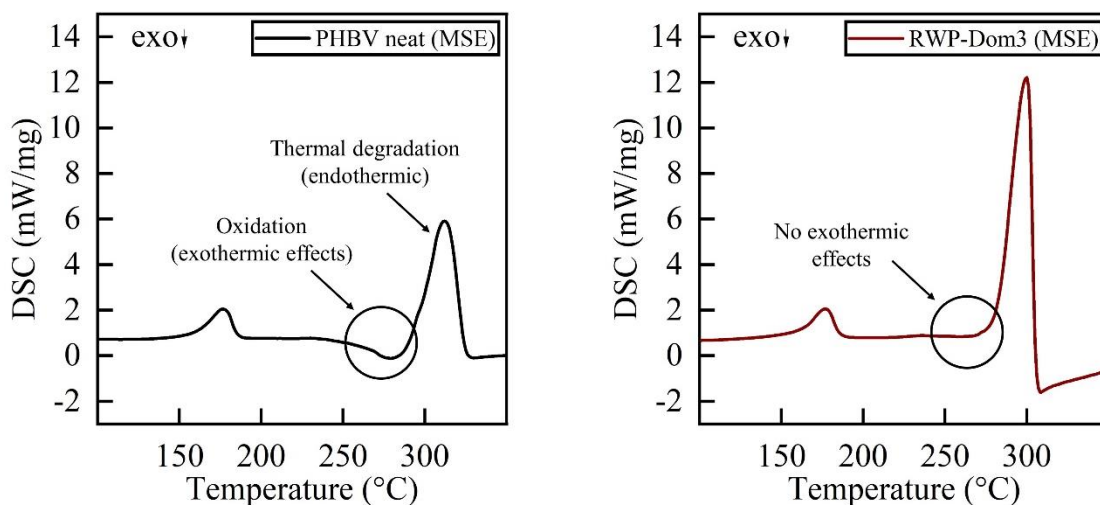


Figure 3: OIT graphs of neat PHBV (left) and PHBV filled with 3 wt.-% RWP-Dom (right) processed with MSE

The antioxidative stabilization is already present at low filler contents of 3 wt.-%, completely suppressing exothermic effects caused by oxidative reactions. Accordingly, the determination of OIT_{off} was not possible for biocomposites with filler contents higher than 2 wt.-% due to the absence of exothermic effects. Besides exothermic effects, the OIT measurements of the neat PHBV materials showed intense endothermic effects, indicating that the thermal degradation was the dominating degradation mechanism of PHBV [4,13]. The increase in thermo-oxidative stability by the biogenic by-products resulted in a superposition of endothermic and exothermic effects due to the prevention of premature thermo-oxidative degradation.

As displayed in Figure 4, the addition of the WP-filler led to an increase in MFR with increasing filler content. This increment may be ascribed to the plasticizing effects of the lipid fractions in the filler in forms of oils and fatty acids in the grape seeds [6]. The gap between the neat PHBV processed with the MSE and TSE was maintained even at higher filler contents, indicating the intensive impact of the extruder type on the MFR of PHBV. This was different for the thermal stability determined using TGA. The gap between the neat PHBV processed with the MSE and TSE disappeared at higher filler contents. Accordingly, the influence of the bio-filler appeared to dominate over the effects of the process on the thermal stability of the materials. However, the biocomposites results confirmed that the dominant degradation mechanism for the MSE was the thermal degradation and thermomechanical degradation in the case of the TSE.

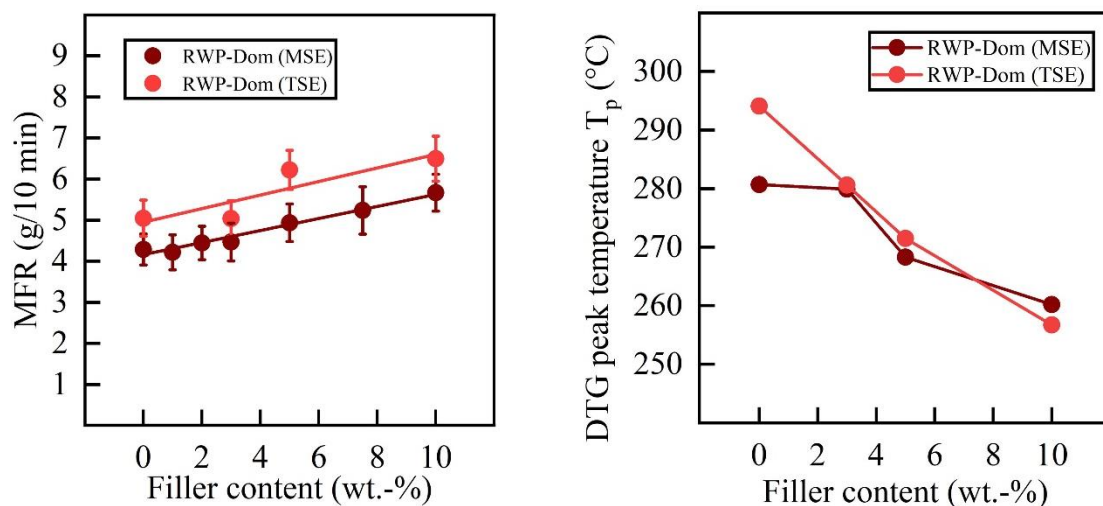


Figure 4: MFR (left) and TGA data (right) with respect to filler content and extruder type

5.3 Evaluation of the mixing quality of the extruder types

The potential of the MSE for use as a miniaturized compounder was investigated by microscopy imaging with image analysis on thin films to determine the key indicators reported in Table 5. Regarding the spatial distribution, the I_δ values for both extruder types were very close to 1 regardless of the filler content. This indicates a discrete and random distribution of the filler particles in the polymer matrix with both extruders [9]. The skewness (β) specifies the asymmetry of the distribution plot around the mean. For both extruders, small values around 0 were obtained, which indicate well-dispersed particles with low clustering and aggregation, and good uniformity of the distribution [9]. Both extruders showed comparable coefficients of variation (v) with slightly lower values for the TSE. With v in the ranges of 0.045–0.102 both extruders show sufficient mixing quality [10]. The degree of disaggregation (k), obtained for filler contents of up to 5 wt.-%, was >1 , demonstrating that due to intense dispersive mixing the mean particle diameter of the filler particles incorporated was smaller than the initial mean particle size. For filler contents of 10 wt.-%, aggregates and agglomerates were formed during

processing, leading to k values slightly below 1 [10,11]. However, this analysis revealed that for the observed material combinations at filler contents up to 10 wt.-%, the mixing quality of the MSE was comparable to the homogeneity achieved by the lab-scale TSE.

Table 5: Key indicators for mixing quality of the extruder types obtained from microscopy imaging

Filler Content (wt.-%)	I_δ^6 (-)	β^7 (-)	v^8 (-)	k^9 (-)
MSE				
3.0	1.005 ± 0.003	0.673 ± 1.446	0.102 ± 0.043	1.144 ± 0.036
5.0	1.006 ± 0.004	-0.818 ± 1.191	0.081 ± 0.025	1.091 ± 0.031
10.0	1.002 ± 0.001	0.495 ± 1.826	0.073 ± 0.029	0.986 ± 0.019
TSE				
3.0	1.001 ± 0.001	-0.921 ± 1.063	0.062 ± 0.009	1.128 ± 0.029
5.0	1.001 ± 0.001	0.053 ± 1.775	0.070 ± 0.019	1.051 ± 0.022
10.0	1.001 ± 0.000	-0.561 ± 1.207	0.045 ± 0.017	0.896 ± 0.048

⁶ Morisita's index; ⁷ skewness; ⁸ coefficient of variation for the mixing quality; ⁹ degree of disaggregation.

5.4 Comparison of the economics of the extruder types

For compounding, the use of the MSE shows multiple economic benefits compared to a lab-scale TSE. Firstly, the investment costs are remarkably lower, representing 5–10% of the costs of a laboratory TSE setup, depending on additional equipment options. Secondly, as mentioned in Table 1, the MSE requires less space and lower minimum amounts of material, leading to further savings in labor and material costs. While the TSE required about 1 kg of material to obtain a batch of at least 50 g for analysis due to machine filling, start-up, and production waste, 100 g was sufficient for the MSE. This advantage of higher material-efficiency for the MSE increases with the number of material combinations used and the material throughput applied on the TSE. This represents a key benefit, especially when considering expensive and/or rare materials. An evaluation of the economics of the extruder types in terms of labor costs was performed by tracking the processing times. Based on experimental experiences during the investigations, the required times for process setup and post-processing as well as the times for material changes and the maximum material throughput achieved are reported in Table 6.

Table 6: Processing times as economical key performance indicators of the MSE and TSE

Stage	Action	MSE (h)	TSE (h)
Single material combinations			
Preparation	Screw configuration	0.50	1.00
	Side feeder setup	-	0.50
	Dosing system setup	-	0.50
Process start-up	Pre-heating and start-up	0.50	0.50
Cleaning	Purging	0.50	0.50
	Disassembling and cleaning of the screw	0.50	1.00
	Cleaning of the extruder	0.50	5.00
Total	Machine preparation and post-processing (t_{pp})	2.50	9.00
Multiple material combinations			
Change of material combination	Cleaning of the hopper	0.15	0.50
	Cleaning of the side feeder	-	0.80
	Purging and re-start	0.50	0.50
Total	Change of material combination (t_{cm})	0.65	1.8
Processing		(kg/h)	(kg/h)
Extrusion	Max. material throughput for stable processing (\dot{m})	0.10	1.70

Based on the tracked processing times, Equations (8) and (9) were used to calculate the break-even material batch sizes above which the use of the TSE is preferable to the MSE.

$$t_s = t_{pp} + \frac{m_b}{\dot{m}} \quad (8)$$

$$t_m = t_{pp} + \frac{m_b \cdot n_b}{\dot{m}} + t_{cm} \cdot (n_b - 1) \quad (9)$$

Where t_s represents the total time for single material combinations (h), t_{pp} represents the total time for machine preparation and post-processing (h), m_b represents the material batch size (kg), \dot{m} represents the maximum material throughput for stable processing (kg/h), t_m represents the total time for multiple material combinations (h), n_b represents the number of material combinations, and t_{cm} represents the total time for the change of material combination (h).

This analysis revealed that especially for small batches up to 700 g of a single material combination, the MSE was more cost- and time-efficient, mainly because of the shorter time required for machine preparation and post-processing. Although the MSE required almost three times less time for changing the material combination, the break-even material batch sizes were reduced with an increasing number of material combinations. The seventeen times higher maximum material throughput for the TSE compensated the longer t_{cm} , leading to break-even material batches of 410, 320, and 240 g for two, three, and five material combinations. However, for frequent material changes and small sample batches, the MSE still represents a preferable option if high material efficiency is required. The reported times account for the specific machines and the material combinations used in this study. These key performance indicators may also vary for different machine configurations (e.g., processing of pre-mixed materials with the TSE without using the side feeder would reduce t_{pp} and t_{cm}). The comparison of the two extruder types used in this study showed that for the investigated materials the MSE represents a considerable alternative to conventional TSE setups. Although higher throughputs of the TSE are beneficial when larger quantities of materials are required, the preparation, cleaning, and process setup are more time-consuming, and more waste is generated. Therefore, from an economical point of view, the MSE is a suitable and efficient alternative to the TSE for applications in research and development. In addition, the MSE can be used as a supplementary option. The advantages of both extruder types can be combined by using the MSE for preliminary experiments and producing only promising materials/material combinations in larger quantities with the TSE, e.g., for tensile test specimens.

5.5 Limitations of the present study and the use of MSEs for compounding

Although this study showed a high potential for the use of the MSE as a small-sized and low-cost compounder, a critical placement of the results in a broader context is required. Compounding polymer materials using a TSE is well-established in the plastics industry. Based on extensive research and practice, its limitations and necessary adaptations for a wide range of applications are well known [10]. The results of this study refer to the specific extruder types and the specific material combination investigated. Sufficient and comparable homogeneity up to a filler content of 10 wt.-% was achieved for the compounding of PHBV and the WP-based bio-filler on both extruders. However, other material combinations and higher filler contents can cause problems such as segregation of pre-mixed materials, particle aggregation, and inhomogeneities, which are common in compounding using single-screw extruders [1,12]. Distler et al. [2] reported a homogeneous distribution of bioactive glass particles with a top cut (d_{95}) $\leq 20 \mu\text{m}$ at filler contents up to 10 wt.-% in a poly(lactic acid) (PLA) matrix. This indicates that low contents of fillers, which tend to agglomerate, can be evenly mixed with an MSE using a powder/powder (matrix/filler) combination. Concerning different matrix material

forms, Domínguez-Robles et al. [3] achieved homogenous materials by using PLA pellets and a lignin powder at filler contents of 0.5–3.0 wt.-%. In this study, the PLA pellets were coated with castor oil to attach the filler particles to the pellets to avoid demixing during processing with the MSE. Díaz-García et al. [1] further developed a novel method to obtain homogeneous composites by encapsulating filler powders for improved control of filler concentration and uniform distribution. These studies demonstrated potential methods to overcome challenges of segregation and inhomogeneities when using an MSE. However, since only low filler contents were used, the question of the performance of the MSE at higher filler contents, as required for masterbatches and highly filled compounds with or using multiple fillers, remains unanswered. Gale [12] described and discussed ways to improve the distributive and dispersive mixing quality of single-screw extruders, enabling compounding with this extruder type for certain applications. However, from a general point of view, he stated that a co-rotating TSE will outperform its single-screwed counterpart in most applications [12], regardless of the extruder dimension (industrial scale or miniaturized). Therefore, a re-evaluation of the MSE compared to the TSE when using different machines and/or other material combinations is mandatory to ensure valid research.

6. CONCLUSION

In conclusion, the MSE represents a considerable material-saving, cost-efficient, small-sized alternative to a lab-scale TSE for compounding small quantities of biocomposites. To achieve reliable powder processing, the insulation, cooling, and feeding of the MSE was modified. For the investigated material combination, the mixing quality achieved on both machines was comparable for filler contents up to 10 wt.-%. Nevertheless, differences were found between the processes in terms of the dominant degradation mechanisms of the investigated PHBV-based biocomposites during processing. While thermomechanical degradation caused by higher shear rates was dominant for the TSE, thermal degradation was the major degradation phenomenon for the MSE due to longer residence times. These differences must be considered when comparing materials processed with both machines. Thermal analysis revealed that the wine-derived biogenic by-products acted as antioxidant stabilizers, preventing thermo-oxidative degradation of the PHBV. Finally, an economical evaluation showed that especially for small quantities and frequent material changes, the MSE is a beneficial option for tasks in research and development, reducing the challenges of bioplastics research and contributing to its progress. However, the common challenges of using industrial single-screw extruders for compounding materials with higher filler contents may also apply to MSEs. Accordingly, future research should evaluate the potential of the MSE compared to the TSE by investigating matrix materials with different melt viscosities and forms, different filler types, and higher filler contents to ensure the transferability of the approach to a broader range of material systems.

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