# Biodegradable PLA/PHBV Polymer Blends for Sustainable Packaging in the Food Industry

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## Abstract

Almost half of the global production of fossil-based polymers is used for food packaging, and their resistance to biodegradation leads to significant environmental impacts. Polymers synthesised from renewable sources have become crucial for the development of sustainable packaging materials, particularly in the food industry. Biodegradable polymers such as poly(lactic acid) (PLA) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) have emerged as promising alternatives to conventional polymers. However, due to the limiting properties of the individual polymers, PLA/PHBV blends have been developed to improve their thermal and barrier performance, and to retain their biodegradability. In this study, the properties of PLA/PHBV polymer blends with varying PLA content were investigated. Thermal properties were analysed using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The morphology of the samples was examined by scanning electron microscopy (SEM), while barrier properties were assessed using the Hoffman method. Changes in chemical structure and interactions between PLA and PHBV were studied by Fourier-transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR). Adhesion-related parameters were indirectly evaluated by measuring surface contact angles and test liquids. The results indicate that PLA/PHBV blends with lower PHBV content exhibit better morphological, thermal, mechanical, and barrier properties than blends with higher PHBV content. The obtained properties of the PLA/PHBV blends provide improved functionality while maintaining environmental compatibility, making them promising formulations for the development of sustainable food packaging.

## Keywords

Polylactic acid (PLA), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), polymer blends, sustainable packaging

## 1 Introduction

The growing global population and increasing demand for materials, together with waste accumulation, have made reducing the negative environmental impact of production imperative.[1,2] To achieve this goal, it is necessary to address the growing volume of single-use packaging waste. According to Eurostat data from 2021, the average amount of packaging waste per person in the EU was 188.7 kg, with non-degradable synthetic polymer materials accounting for around 20 %. Approximately 76 % of polymeric waste ends up in landfills and ecosystems, where it remains for hundreds of years without decomposing.[3,4] A possible alternative to synthetic packaging polymers are biodegradable, non-toxic polymer materials that can be safely disposed of in the environment, where they decompose into biomass within an acceptable period of time.[5] Due to their generally inferior mechanical and barrier properties, they need to be formulated into blends to achieve the performance required for packaging applications.

Owing to its good processability, durability, mechanical strength, and transparency, poly(lactic acid) (PLA) is one of the most widely used commercial biopolymers.[6] PLA

is an aliphatic polyester derived from lactic acid (LA). As lactic acid is produced by microbial fermentation of agricultural by-products, PLA represents a suitable alternative to petrochemical-derived products and promotes a circular economy model.[7] Although PLA is among the most promising biopolymers for packaging applications, its use in food packaging is limited by its relative brittleness, low impact resistance, and moderate barrier properties, which are insufficient for preserving food quality and extending shelf life.[8] These limitations necessitate material modification to broaden PLA's applicability in packaging systems. The incorporation of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) into PLA matrices offers an effective approach to addressing these shortcomings.[9] PHBV is a biodegradable and biocompatible thermoplastic polyester[10], a copolymer of 3-hydroxyvalerate (3HV) monomers and 3-hydroxybutyrate (3HB) monomers. The higher 3HV monomer portion improves PHBV's flexibility, toughness, and processability, while it decreases crystallinity and brittleness, thus retaining suitable strength for packaging applications. Its good barrier properties against moisture and gases make PHBV highly attractive for the packaging industry.[11] However, as reported by *Jost et al.*, PLA and PHBV are generally considered partially miscible or immiscible systems, with their degree of compatibility strongly dependent on blend composition, processing conditions, and the hydroxyvalerate content of PHBV.[12] PLA/PHBV blends with compositions of 75/25, 50/50, and 25/75 prepared by melt-mixing, as reported by *Zembouai et al.*,[13] exhibited a two-phase morphology with limited interfacial

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adhesion across the entire composition range. These results are further supported by the presence of two distinct glass transition temperatures and separate melting peaks corresponding to each polymer component.[14] Insufficient miscibility often leads to phase separation and weak interfacial adhesion, which can limit mechanical, thermal, and barrier performance. Enhancing the miscibility of PLA/PHBV blends is therefore essential to further improve their functional properties. A critical first step toward this goal is identifying the blend composition that exhibits the highest degree of miscibility, which can subsequently be optimised through targeted strategies such as the incorporation of compatibilisers to improve interfacial interactions and enhance material performance.

Accordingly, this work investigates PLA/PHBV polymer blends to identify the composition that exhibits the highest degree of miscibility, barrier performance, and thermal stability. Changes in chemical structure and interactions between PLA and PHBV were examined using Fourier transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR). Thermal characteristics of the blends were assessed using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Adhesion parameters were estimated indirectly by measuring contact angles between the prepared blends and the testing liquids. The sample morphology was observed through scanning electron microscopy (SEM) and a thorough evaluation of the barrier properties was performed.

# 2. Experimental

## 2.1 Materials

PLA/PHBV polymer blends with different polymer contents were prepared using polylactic acid (PLA), Luminy LX175, produced by TotalEnergies Corbion (Netherlands) and poly(3-hidroxybutyrate-co-3-hydroxyvalerate) (PHBV), ENMAT Y1000P, produced by TianAn Biologic Materials (China).

## 2.2 Preparation of PLA/PHBV polymer blends

PLA/PHBV polymer blends were prepared in specific weight ratios, as shown in Table 1. Pure PLA and PHBV were used as control samples. The weighed polymer granules were homogenised in a Brabender internal mixer preheated to 170 °C. During the initial softening stage, the screw speed was reduced to 20 rpm to allow controlled melting. After the material reached viscoelastic state, the blend was mixed for 10 min at a screw speed of 60 rpm, in accordance with the melt-mixing conditions reported by *Mofokeng et al.*[15]

To make the samples suitable for characterisation, the obtained blends were compression-moulded into plates and films using a Fontune Holland hydraulic press (pressed at 20 kPa and 170 °C for 5 min) and cooled on a Dake Model 44-226 press to room temperature.

Table 1 – Mass ratio of the prepared PLA/PHBV blends
Tablica 1 – Maseni omjeri pripremljenih PLA/PHBV mješavina

| Sample<br>Oznaka uzorka | PLA/wt.% | PHBV/wt.% |
|---|---|---|
| PLA | 100 | – |
| PHBV | – | 100 |
| PLA/PHBV 95/5 | 95 | 5 |
| PLA/PHBV 90/10 | 90 | 10 |
| PLA/PHBV 55/45 | 55 | 45 |
| PLA/PHBV 50/50 | 50 | 50 |

## 2.3 Sample characterisation

### 2.3.1 Fourier transform infrared spectroscopy with attenuated total reflectance (ATR-FTIR)

The characteristic functional groups of PLA and PHBV were identified using Fourier transform infrared spectroscopy with attenuated total reflectance (ATR-FTIR) on a PerkinElmer Spectrum One FTIR-ATR spectrophotometer. The spectra were collected at room temperature over the range of 4000–650 cm$^{-1}$ with a resolution of 4 cm$^{-1}$ and 32 scans per sample.

### 2.3.2 Contact angle measurement

The total surface energy and its polar and dispersive components were indirectly determined by contact angle measurements using a DataPhysics OCA 20 goniometer with three testing liquids: water, formamide, and diiodomethane. Each measurement was repeated ten times using 2 μl of the testing liquid. The surface energy components of the test liquids are given in Table 2.

Table 2 – Surface free energy component values of the test liquids
Tablica 2 – Vrijednosti komponenata slobodne energije površine za navedene testne kapljevine

| Test liquids<br>Testne kapljevine | $\gamma^p$/mJ m$^{-2}$ | $\gamma^d$/mJ m$^{-2}$ | $\gamma$/mJ m$^{-2}$ |
|---|---|---|---|
| water | 51.00 | 21.80 | 72.80 |
| formamide | 19.00 | 39.00 | 58.00 |
| diiodomethane | 0.00 | 50.80 | 50.08 |

$\gamma^p$ – polar component; $\gamma^d$ – dispersion component; $\gamma$ – surface tension

The Owens-Wendt-Rabel-Kaelble (OWRK) and Wu models were used to calculate surface free energy using polar and dispersive energy components in Eqs. (1) and (2), respectively. From the obtained polar and dispersive components of PLA and PHBV samples, adhesion parameters such as thermodynamic work of adhesion ($W_{12}$), and spreading coefficient ($S_{12}$), were also calculated using Eqs. (3) and (4), respectively.

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^d \gamma_2^d} - 2\sqrt{\gamma_1^p \gamma_2^p} \qquad (1)$$

$$\gamma_{12} = \gamma_1 + \gamma_2 - \frac{4\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} - \frac{4\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p} \qquad (2)$$

$$W_{12} = \gamma_1 + \gamma_2 - \gamma_{12} \qquad (3)$$

$$S_{12} = \gamma_1 - \gamma_2 - \gamma_{12} \qquad (4)$$

where $\gamma^p$ represents the polar component; $\gamma^d$ represents the dispersive components; $\gamma_{12}$ is the interfacial tension between materials 1 and 2; $\gamma_1$ and $\gamma_2$ are the surface tension values of the two contacting components in the blends.

### 2.3.3 Differential scanning calorimetry (DSC)

Phase transitions were analysed using a Mettler Toledo DSC 3 Star System calorimeter. The thermal programme included two heating cycles and one cooling cycle between $-60\ °C$ and $200\ °C$ at a rate of $10\ °C\,min^{-1}$. The first heating cycle was used to eliminate the sample's thermal history, while the cooling and second heating cycles were used for evaluation. All measurements were performed under a nitrogen atmosphere. The degree of crystallinity ($\chi_c$) for each sample was calculated using the Eq. (5):

$$\chi_c\ [\%] = \frac{\Delta H_m}{\Delta H_m^0 \cdot w(\text{polymer})} \cdot 100 \qquad (5)$$

where $\Delta H_m$ represents the melting enthalpy of the polymer obtained from the second heating cycle from the DSC analysis, $\Delta H_m^0$ represents the melting enthalpy for a 100 % crystalline polymer. Melting enthalpy for a 100 % crystalline PLA values $93.7\ J\,g^{-1}$, whereas for PHBV it values $109\ J\,g^{-1}$.[14,15]

### 2.3.4 Thermogravimetric analysis (TGA)

Thermal stability and decomposition behaviour of the tested samples were evaluated using Mettler Toledo TGA/DSC 3+ Star System under a nitrogen atmosphere. The temperature range was set from 25 to 500 °C, with a constant heating rate of $10\ °C\,min^{-1}$.

### 2.3.5 Scanning electron microscopy (SEM)

The microstructure of the fracture surface after cryogenic breakage was examined using a high-resolution microscope, Tescan Vega Series 3. To enhance the conductivity, samples were sputter-coated with gold and palladium particles. SEM imaging was conducted under high vacuum conditions at an accelerating voltage of 20 kV. Fracture surfaces were observed at a magnification of $500\times$ and the images are presented in the results section.

### 2.3.6 Water vapour permeability

Water vapour permeability (WVP) was evaluated using a custom-built Herfeld's apparatus in accordance with DIN

53333. A circular polymer film ($\varnothing\ 55$ mm) was sealed over the top of a glass vessel containing 50 ml of distilled water. The vessel was covered with a 36 mm diameter opening and placed inside a desiccator containing 97 wt.% sulphuric acid for 48 h. The weight of the assembly was measured before the experiment ($m_0$), after 24 h ($m_1$), and after 48 h ($m_2$). WVP was subsequently calculated according to Eq. (6).

$$WVP = \frac{\left[ m_0 - \left( \dfrac{m_1 + m_2}{2} \right) \right]}{A} \qquad (6)$$

## 3 Results and discussion

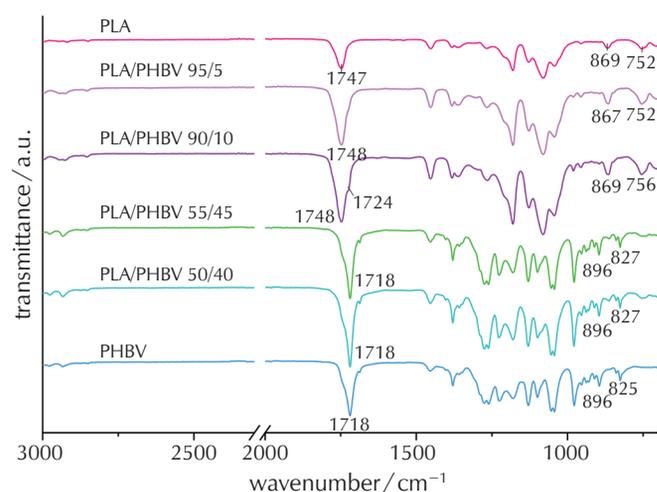### 3.1 Fourier transform infrared spectroscopy (FTIR)



*Fig. 1* – ATR-FTIR spectra of prepared PLA/PHBV polymer blends and control samples
*Slika 1* – ATR-FTIR spektri pripremljenih PLA/PHBV polimernih mješavina i kontrolnih uzoraka

The polymer blends exhibited characteristic transmittance bands of pure PLA and PHBV (Fig. 1). In the PLA/PHBV blends spectra, no new transmittance bands were observed, indicating the absence of chemical reactions during blending, and suggesting that the interactions between PLA and PHBV were electrostatic in nature, occurring between $\alpha$-methylene groups of PHBV and carboxyl groups of PLA.[16] Due to these interactions between PLA and PHBV, a shift in the transmittance bands towards lower wavenumbers was observed with increasing PHBV content. The transmittance band of the carbonyl group in PLA was observed at $1747\ cm^{-1}$ and at $1718\ cm^{-1}$ for carbonyl group in PHBV. In PLA/PHBV samples, as the PHBV content increased (PLA/PHBV = 55/45 and 50/50), the carbonyl transmittance band of PLA shifted from $1747\ cm^{-1}$ towards $1718\ cm^{-1}$ due to changes in the local molecular environment during crystallisation induced by the interactions between PLA and PHBV.[16]

In addition, the transmittance band observed at $1724\ cm^{-1}$ can be attributed to overlapping carbonyl stretching vi-

brations of PLA and PHBV, with the contribution of the PHBV phase being shifted.[13] Literature reports[17] confirm their total immiscibility based on atomic force microscopy-infrared (AFM-IR) measurements. However, the use of PLA and PHBV provided by different suppliers, as well as the different preparation conditions and measuring techniques should be taken into the account.[17] Furthermore, the intensity of the transmittance bands corresponding to C−O−C bonds at 869 cm$^{-1}$ and C−H bonds at 752 cm$^{-1}$ was higher compared to the pure PHBV sample, reflecting changes in the helical structure of PHBV upon the addition of PLA, which led to reduced crystallinity and the formation of amorphous regions. These results are consistent with previous studies.[17]

## 3.2 Contact angle measurement

Table 3 – Contact angle of the samples measured with test liquids
Tablica 3 – Rezultati mjerenja kontaktnog kuta ispitivanih uzoraka s testnim kapljevinama

| Sample Uzorak | Contact angle Kontaktni kut, $\theta/°$ | | |
|---|---|---|---|
| | Water Voda | Formamide Formamid | Diiodomethane Dijodometan |
| PLA | 79.8 ± 1.8 | 83.3 ± 2.6 | 62.7 ± 1.0 |
| PHBV | 84.3 ± 1.9 | 73.4 ± 1.8 | 49.6 ± 1.9 |
| PLA/PHBV 95/5 | 75.4 ± 1.6 | 56.2 ± 1.2 | 43.9 ± 1.3 |
| PLA/PHBV 90/10 | 71.3 ± 2.2 | 52.0 ± 2.0 | 38.4 ± 2.9 |
| PLA/PHBV 55/45 | 75.5 ± 1.7 | 50.7 ± 2.9 | 38.9 ± 1.4 |
| PLA/PHBV 50/50 | 69.7 ± 2.0 | 51.2 ± 1.0 | 36.5 ± 1.5 |

Measurement of the contact angles of the prepared blends with water, formamide, and diiodomethane (Table 3) revealed that PLA and PHBV exhibited higher contact angles with polar liquids than with the non-polar diiodomethane, due to the pronounced dispersive energy component. Additionally, a contact angle close to 90° confirmed the hydrophobic character of both polymers, as reported in previous studies.[18,19] The contact angles of the prepared PLA/PHBV blends were lower than those of the individual components, indicating increased surface energy and improved wettability due to the partial miscibility of PLA and PHBV.

Among the blends, PLA/PHBV 95/5 showed low contact angles with formamide and diiodomethane, and a favourable contact angle with water, providing the best balance between polar and dispersive interactions and wettability, making it the most suitable for packaging applications (Table 3). This trend was further confirmed by the Wu and OWRK models, which revealed that PLA/PHBV 95/5 had the highest total surface energy (44.41 mJ m$^{-2}$ and 40.89 mJ m$^{-2}$, respectively) and increased polar and dispersive components compared to the other blends (Table 4).

The reduced hydrophobicity of the prepared blends should be considered when evaluating their suitability for food packaging, as many bacteria preferentially adhere to more hydrophilic surfaces, where hydrogen bonding and hydration layer effects facilitate initial adhesion and biofilm formation.[18] When assessing adhesion between components, surface free energy, thermodynamic work of adhesion, and spreading coefficient should be considered. The calculated interfacial parameters between PLA and PHBV are shown in Table 5, indicating favourable adhesion characteristics within the blend system. The low interfacial surface free energy (1.68 mJ m$^{-2}$) and high thermodynamic work of adhesion (54 mJ m$^{-2}$) suggest strong interfacial interactions and compatibility, which is essential for good mechanical integrity. Although the negative spreading coefficient (−9.39 mJ m$^{-2}$) indicates that complete spreading did not occur spontaneously, its relatively small magnitude confirms partial wetting and stable interfacial contact. These results demonstrate that PLA/PHBV blends, particularly the

Table 4 – Values of the dispersive ($\gamma^d$) and polar components ($\gamma^p$), and the total surface free energy ($\gamma$) of PLA/PHBV blends according to the OWRK and Wu models
Tablica 4 – Vrijednosti disperzijske ($\gamma^d$) i polarne komponente ($\gamma^p$) te ukupne slobodne površinske energije ($\gamma$) PLA/PHBV mješavina prema OWRK i Wu modelu

| Sample Uzorak | Surface free energy Slobodna površinska energija | | | | | |
|---|---|---|---|---|---|---|
| | Wu model | | | OWRK model | | |
| | $\gamma^d$/mJ m$^{-2}$ | $\gamma^p$/mJ m$^{-2}$ | $\gamma$/mJ m$^{-2}$ | $\gamma^d$/mJ m$^{-2}$ | $\gamma^p$/mJ m$^{-2}$ | $\gamma$/mJ m$^{-2}$ |
| PLA | 23.98 | 8.27 | 32.25 | 20.61 | 7.13 | 27.74 |
| PHBV | 31.65 | 5.36 | 37.01 | 27.43 | 3.93 | 31.36 |
| PLA/PHBV 95/5 | 34.94 | 9.48 | 44.41 | 35.18 | 5.72 | 40.89 |
| PLA/PHBV 90/10 | 36.86 | 10.8 | 47.63 | 37.46 | 6.77 | 44.23 |
| PLA/PHBV 55/45 | 37.79 | 9.26 | 47.05 | 38.75 | 5.03 | 43.78 |
| PLA/PHBV 50/50 | 37.30 | 11.29 | 48.59 | 37.98 | 7.23 | 45.21 |

| Sample Uzorak | $\gamma_{PLA/PHBV}$/mJ m$^{-2}$ | $W$/mJ m$^{-2}$ | $S$/mJ m$^{-2}$ |
|---|---|---|---|
| PLA/PHBV | 1.68 | 53.95 | −9.35 |

95/5 composition, can form materials with effective interfacial adhesion, supporting the development of biodegradable packaging with improved structural and functional properties.

## 3.3 Differential scanning calorimetry (DSC)

DSC analysis provided insight into the thermal behaviour and crystallinity of the prepared samples, with corresponding thermograms shown in Fig. 2 and thermal parameters summarised in Table 6. Neat PLA exhibited a moderate degree of crystallinity (26.29 %), a glass transition temperature at 60.49 °C, a pronounced cold crystallisation peak at 116.88 °C, and a melting temperature of 151.38 °C,

which is characteristic of semi-crystalline PLA with slow crystallisation kinetics.[20] In contrast, neat PHBV showed a single melting peak at 171.87 °C and a very high degree of crystallinity (89.54 %), indicating rapid crystallisation during cooling and a highly ordered crystalline structure. This behaviour is consistent with previous studies, and aligns with the ordered structure of the PHBV polymer chains. The thermal behaviour of PLA/PHBV blends is composition-dependent. Blends with low PHBV content (PLA/PHBV 95/5 and 90/10) exhibited DSC profiles similar to neat PLA, characterised by a single melting endotherm close to the PLA melting temperature. For the blends with higher PHBV content (PLA/PHBV 55/45 and 50/50), two distinct melting peaks corresponding to the PLA and PHBV phases were observed, confirming phase separation and immiscibility. Although the overall crystallinity of these blends exceeded 60 %, the degree of crystallinity of the PHBV phase ($\approx$ 60–61 %) was markedly lower than that of neat PHBV. This reduction suggests that, similar to the PLA phase, PHBV crystallisation was also hindered in the blend due to confinement effects and restricted chain mobility imposed by the presence of the second polymer phase. In general, the degree of crystallinity of all the prepared blends decreased with increasing PHBV content. This corresponds to the changes in contact angles between the prepared blends and water, where increased wettability was observed with higher PHBV content. Table 3 shows a decrease in contact angle values, which can be explained
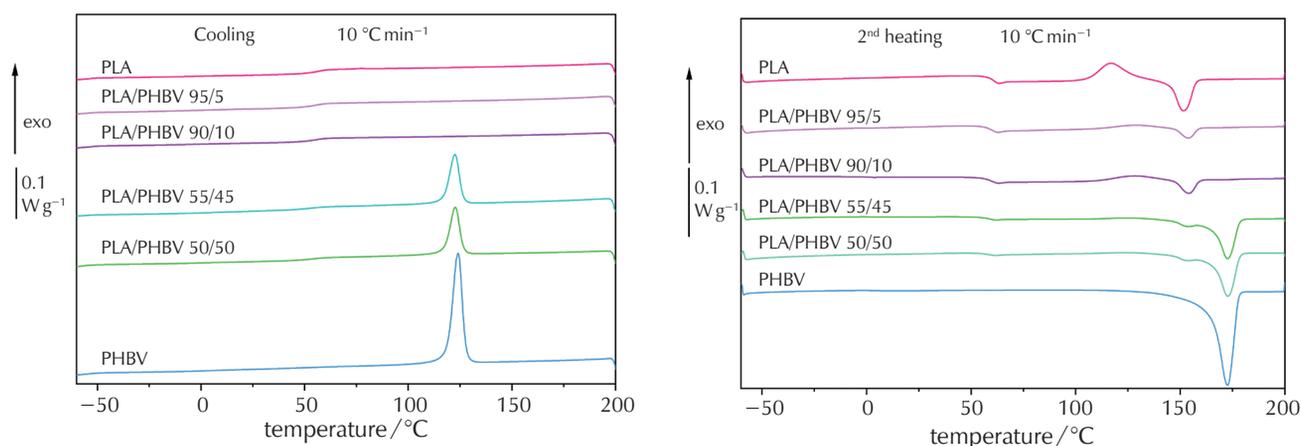


*Fig. 2* – DSC cooling and heating curves of the tested samples
*Slika 2* – DSC krivulja hlađenja i zagrijavanja ispitivanih uzoraka

*Table 6* – DSC analysis results
*Tablica 6* – Rezultati DSC analize

| Samples Uzorci | $T_{cc(PLA)}$/°C | $\Delta H_{cc(PLA)}$/J g$^{-1}$ | $T_{c(PHBV)}$/°C | $\Delta H_{c(PHBV)}$/J g$^{-1}$ | $T_{g(PLA)}$/°C | $T_{m1(PLA)}$/°C | $T_{m2(PHBV)}$/°C | $\Delta H_{m1(PLA)}$/J g$^{-1}$ | $\Delta H_{m2(PHBV)}$/J g$^{-1}$ | $\chi_{c(PLA)}$/% | $\chi_{c(PHBV)}$/% |
|---|---|---|---|---|---|---|---|---|---|---|---|
| PLA | 116.88 | 28.74 | – | – | 60.49 | 151.38 | – | 24.64 | – | 26.96 | – |
| PHBV | – | – | 125.10 | 88.86 | – | – | 171.87 | – | 97.60 | – | 89.54 |
| PLA/PHBV 95/5 | 128.81 | 7.67 | – | – | 59.75 | 153.88 | – | 6.30 | – | 7.08 | – |
| PLA/PHBV 90/10 | 128.10 | 11.14 | – | – | 59.51 | 153.96 | – | 8.86 | – | 10.05 | – |
| PLA/PHBV 55/45 | 130.76 | 5.07 | 123.27 | 38.57 | 58.34 | 152.70 | 172.42 | 1.48 | 29.68 | 2.87 | 60.51 |
| PLA/PHBV 50/50 | – | – | 123.05 | 38.65 | 56.48 | 152.42 | 172.47 | 1.22 | 33.25 | 2.60 | 61.01 |

by reduced crystallinity and a higher content of amorphous phase in the matrix.

The DSC results therefore confirm that while PLA-rich blends retain PLA-like thermal behaviour, PHBV-rich blends are governed by PHBV crystallisation and immiscibility effects, in agreement with literature findings.[17,21,22]

### 3.4 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was conducted to investigate the thermal stability and behaviour of neat PLA, neat PHBV, and their blends. The results are presented in Fig. 3 and summarised in Table 7. Neat PLA exhibited a single-step degradation process, with thermal decomposition initiating at a high onset temperature ($T_{onset}$ = 316.83 °C) and reaching a maximum degradation rate at 372.35 °C. These results are consistent with previous studies, confirming high thermal stability of PLA. In contrast, neat PHBV degraded significantly earlier, with an onset at 252.20 °C

and a maximum degradation rate at 292.20 °C, leaving no residue. All PLA/PHBV blends exhibited a two-step degradation behaviour, as confirmed by two distinct DTG peaks. The first degradation step, occurring at approximately 298–302 °C, is attributed to PHBV degradation, while the second step at around 369–371 °C corresponds to PLA decomposition. This behaviour confirmed the immiscible nature of the blends which aligns with previous reports.[22] As shown in Table 7, increasing PLA content slightly enhanced the thermal stability of the PHBV phase, with a noticeable increase in characteristic degradation temperatures observed for the blend containing 5 wt.% PHBV. Overall, the TGA results support that PLA provides structural thermal stability within the blends, while PHBV contributes to early decomposition, lowering the processing range. However, all compositions examined maintained sufficient thermal resistance above 230 °C, which is adequate for common melt-processing operations for food packaging applications[23]. The highest thermal stability was observed in samples with the highest PLA content (PLA/PHBV 90/10 and PLA/PHBV 95/5).
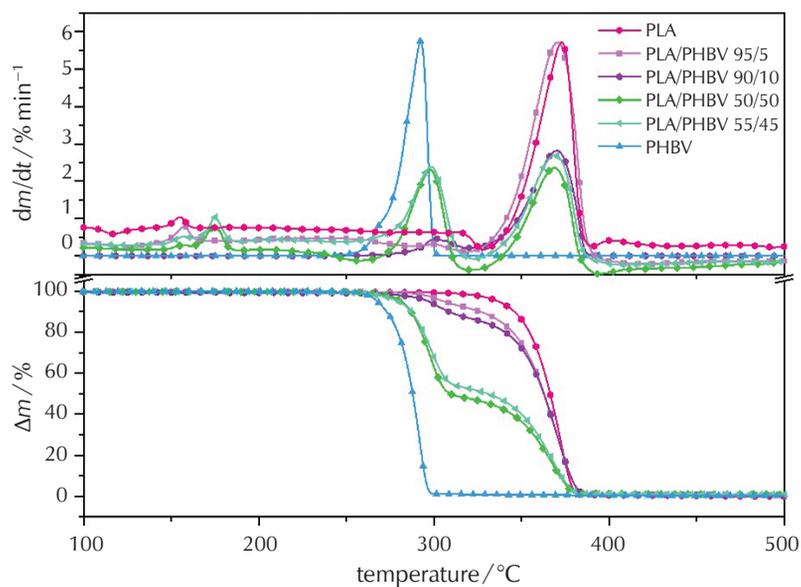


*Fig. 3* – DTG and TG curves for neat PLA and PHBV and their blends
*Slika 3* – DTG i TG krivulje za čisti PLA i PHBV te njihove mješavine

*Table 7* – Thermogravimetric analysis results
*Tablica 7* – Rezultati termogravimetrijske analize

| Sample Uzorak | TG | | | | DTG | | |
|---|---|---|---|---|---|---|---|
| | $T_{onset1}$/°C | $T_{final1}$/°C | $T_{onset2}$/°C | $T_{final2}$/°C | $R_{700\,°C}$/% | $T_{max1}$/°C | $T_{max2}$/°C |
| PLA | 316.83 | 423.50 | – | – | 0.4732 | – | 372.35 |
| PHBV | 252.20 | 302.92 | – | – | 0.00 | 292.20 | – |
| PLA/PHBV 95/5 | 290.31 | 316.11 | 324.83 | 392.17 | 1.3288 | 300.99 | 370.59 |
| PLA/PHBV 90/10 | 273.33 | 322.67 | 336.67 | 387.33 | 0.5232 | 301.70 | 369.50 |
| PLA/PHBV 55/45 | 265.40 | 312.57 | 325.17 | 393.33 | 1.4220 | 298.50 | 369.52 |
| PLA/PHBV 50/50 | 264.67 | 321.57 | 328.50 | 388.83 | 1.4505 | 298.20 | 369.21 |

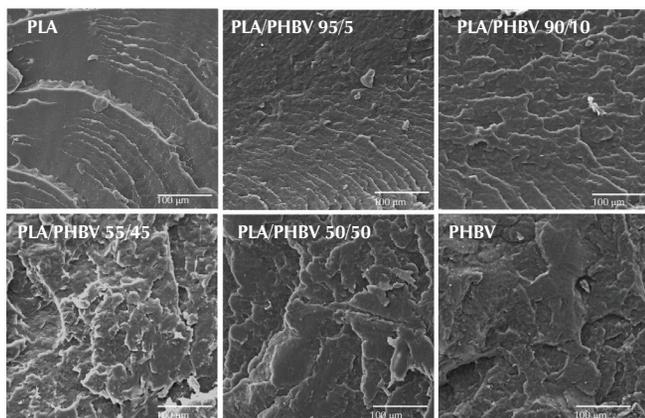## 3.5 Scanning electron microscopy (SEM)



*Fig. 4* – SEM micrographs of the samples at 500× magnification; white line represents a scale of 100 μm
*Slika 4* – SEM mikrografije uzoraka pri povećanju 500×; bijela linija predstavlja skalu od 100 μm
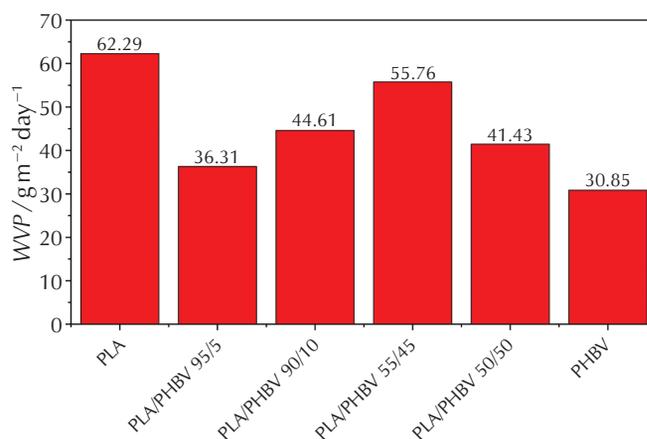


*Fig. 5* – Water vapour permeability (*WVP*) of prepared PLA/PHBV polymer blends
*Slika 5* – Propusnost vodene pare (*WVP*) pripremljenih PLA/PHBV polimernih mješavina

On the SEM micrograph of the control PLA sample, an uneven fracture surface was observed, reflecting the sample's brittleness and stiffness.[24] Compared to PHBV, PLA is a harder and tougher material with a smoother surface. In contrast, the SEM micrograph of the PHBV fracture surface revealed irregularly distributed, non-uniform, and layered structures of a tough and ductile material.[23] SEM micrographs of the fracture surfaces of the polymer blend samples with lower PHBV content (PLA/PHBV 95/5 and PLA/PHBV 90/10) exhibited smoother surfaces due to the dominant influence of the prevailing structure typical for PLA and the finer dispersion of PHBV within the PLA matrix. Among these, the PLA/PHBV 95/5 blend exhibited the most uniform and compact fracture surface, indicating the best interfacial morphology and surface quality.

As the PHBV content increased (PLA/PHBV 55/45 and PLA/PHBV 50/50), clear phase separation and poor interfacial adhesion became evident, pointing to immiscibility between the two polymers. Blends with lower PHBV content, owing to their uniform structure, are likely to exhibit better mechanical integrity and barrier properties, making them more suitable for packaging applications. In contrast, immiscible blends with high PHBV content may suffer from reduced mechanical performance due to higher phase separation and the higher proportion of brittle PHBV structure in the matrix. This observation is consistent with previous studies on similar blends.[20] However, their limited use can potentially be broadened through the addition of compatibilisers or other additives.

## 3.5 Water vapour permeability

Barrier properties are an important parameter in food packaging production, where it is desirable for the packaging material to exhibit low water vapour permeability to prevent product damage caused by moisture.[22] The PLA control sample exhibited higher WVP (62.29 g m$^{-2}$ day$^{-1}$) compared to that of the PHBV control

sample (30.85 g m$^{-2}$ day$^{-1}$). This result corresponds with the previously confirmed higher hydrophobicity of PHBV, as indicated by water contact angle measurements. Since PLA is semi-crystalline, it is expected that the crystalline regions in the polymer structure hinder the diffusion of water vapour through the material.[22] Furthermore, the WVP values of all tested PLA/PHBV blends fell between those of pure PHBV and PLA. All blends showed improved WVP compared to pure PLA, with PLA/PHBV 95/5 exhibiting the lowest WVP among the blends, and therefore, the best barrier performance. This is consistent with the compact surface observed for the PLA/PHBV 95/5 blend, which restricts water molecule penetration. These results also align with contact angle measurements, where the PLA/PHBV 95/5 blend exhibited the highest water contact angle, indicating the lowest surface wettability. On the other hand, the PLA/PHBV 55/45 blend showed the poorest barrier properties, which can be attributed to the mentioned high phase separation observed in SEM analysis, resulting in increased water permeability.[25] However, WVP values remained relatively high, indicating relatively poor barrier properties.

## 4 Conclusion

PLA/PHBV polymer blends were successfully prepared and characterised to determine their potential as food packaging materials. FTIR analysis confirmed the absence of chemical reactions during blending, with spectral shifts indicating physical interactions between PLA and PHBV. Contact angle measurements indicated increased wettability and higher surface energy, implying good compatibility. DSC and TGA results showed that crystallinity varies with composition while all blends maintained thermal stability above 230 °C. SEM analysis indicated morphology changes, where blends with lower PHBV content showed a smoother fracture surface, while blends with high PHBV content showed more layered structures. The morphological homogeneity of the blends further supported the

physical compatibility of blends with lower PHBV content, observed in FTIR and contact angle measurements. All PLA/PHBV blends exhibited reduced water vapour permeability compared to pure PLA, with values falling between those of the neat components. Among the prepared polymer blends, the PLA/PHBV 95/5 blend exhibited the most favourable overall performance, combining improved surface properties, homogeneous morphology, adequate thermal stability, and the lowest water vapour permeability. These findings suggest that the PLA/PHBV 95/5 blend offers a promising balance of thermal and barrier performance, making it a potential candidate for sustainable and biodegradable food packaging applications. Further research should focus on evaluating biodegradability and mechanical performance under simulated food packaging conditions, as well as improving barrier properties, particularly through enhancing the miscibility between PLA and PHBV using suitable compatibilisers to achieve improved interfacial adhesion and overall performance.

## List of abbreviations and symbols
## Popis kratica i simbola

PLA — polylactic acid
— poli(mliječna) kiselina

PHBV — poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
— poli(hidroksibutirat-ko-3-hidroksivalerat)

$\gamma$ — surface free energy (total), mJ m$^{-2}$
— slobodna površinska energija, mJ m$^{-2}$

$W$ — thermodynamic work of adhesion, mJ m$^{-2}$
— termodinamički rad adhezije, mJ m$^{-2}$

$S$ — spreading coefficient, mJ m$^{-2}$
— koeficijent razlijevanja, mJ m$^{-2}$

$\chi$ — degree of crystallinity, %
— stupanj kristalnosti, %

$\Delta H_m$ — melting enthalpy, J g$^{-1}$
— entalpija taljenja, J g$^{-1}$

$\Delta H_{cc}$ — cold crystallisation enthalpy, J g$^{-1}$
— entalpija hladne kristalizacije, J g$^{-1}$

$\Delta H_c$ — crystallisation enthalpy, J g$^{-1}$
— entalpija kristalizacije, J g$^{-1}$

$T_g$ — glass transition temperature, °C
— temperatura staklastog prijelaza, °C

$T_m$ — melting temperature, °C
— temperatura taljenja, °C

$\theta$ — contact angle, °
— kontaktni kut, °

$A$ — surface area of film, mm$^2$
— površina filma, mm$^2$

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# SAŽETAK

## Biorazgradljive PLA/PHBV polimerne mješavine za održivu ambalažu u prehrambenoj industriji

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Gotovo polovica svjetske proizvodnje polimera na osnovi fosilnih goriva upotrebljava se za ambalažu hrane, a njihova otpornost na biorazgradnju i pretjerana akumulacija dovodi do značajnih negativnih utjecaja na okoliš. Polimeri sintetizirani iz obnovljivih izvora postali su ključni za razvoj održivih ambalažnih materijala, posebice u prehrambenoj industriji. Biorazgradivi polimeri poput poli(mliječne kiseline), PLA i poli(3-hidroksibutirat-*co*-3-hidroksivalerata), PHBV pokazali su se kao obećavajuće zamjene konvencionalnim polimerima. Međutim, zbog ograničenih svojstava pojedinačnih polimera razvijaju se PLA/PHBV mješavine s ciljem poboljšanja toplinskih i barijernih svojstava uz očuvanje biorazgradljivosti. Stoga, u ovom su radu istražena svojstva polimernih smjesa PLA/PHBV u različitim omjerima. Toplinska svojstva analizirana su diferencijalnom pretražnom kalorimetrijom (DSC) i termogravimetrijskom analizom (TGA). Morfologija uzoraka istražena je pretražnim elektronskim mikroskopom (SEM), a barijerna svojstva metodom po Herfeldu. Promjene u kemijskoj strukturi te kemijske interakcije PLA i PHBV istražene su infracrvenom spektroskopijom s Fourierovom transformacijom s prigušenom totalnom refleksijom (FTIR-ATR). Parametri adhezije indirektno su procijenjeni mjerenjem kontaktnog kuta površine polimera i testnih kapljevina. Dobiveni rezultati pokazuju da polimerne mješavine PLA/PHBV s nižim udjelom PHBV posjeduju poboljšana morfološka, toplinska, mehanička i barijerna svojstva. Dobivena svojstva PLA/PHBV mješavina nude poboljšanu funkcionalnost uz ekološku prihvatljivost, što ih čini perspektivnim formulacijama za razvoj održive prehrambene ambalaže.