Recycling possibilities of bioplastics based on PLA/PHB blends

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ABSTRACT

The study is focused on modelling the evaluation of recyclability of the biodegradable blend using multiple extrusion of selected composition of PLA/PHB blend which had been more deeply studied before. It was shown that the multiple extrusion reduces viscosity of the tested blend due to multiple thermomechanical stresses and the material was partially degraded. Partial degradation was demonstrated by measuring of molecular characteristics. The degree of degradation of the tested material was determined with relatively high accuracy after creating a colour space/viscosity. Multiple processing and subsequent degradation of the tested material did not negatively affect thermal properties, as well as strength characteristics of the blend. It was concluded that the biodegradable polymer blend of the PLA/PHB type is suitable for multiple processing and material recycling can be applied for this type of bioplastics.

1. Introduction

In the last decades, modern living conditions have led to a dramatic increase of the consumption of polymers (especially plastics). This continued increase in the use of plastics has brought along an increase of amount of plastics in the waste stream motivating greater interest in recycling and reuse of plastics [1]. Nearly 448 million tons of plastics which are produced every year consume about 8% of the world's fossil resources. If the current strong increase in plastic consumption continues as expected, the plastic sector will use 20% of total crude oil consumption by 2050 [2]. Ecological aspects together, as well as rising raw material prices cause a higher utilization of renewable raw materials for a plastics production [3].

Logically, biodegradable materials from renewable sources are a very important option in achieving the goals of sustainable development and reducing negative environmental impact. The advantage of biodegradable materials from renewable sources is especially their biodegradation in biologically active environment and their contribution in lowering carbon footprint. Biodegradable plastics have a wide range of applications, mostly in packaging and agriculture, as well as, due to their biocompatibility, in the field of biocompatible biomaterials. The most common biodegradable plastics are polymer blends which contain thermoplastic starch (TPS) and aliphatic/aromatic polyesters such as

polylactic acid (PLA), polycaprolactone (PCL), polybutylene adipate terephthalate (PBAT) and polyhydroxybutyrate (PHB) [4,5].

PLA, which benefits from origin from renewable sources and is biodegradable in the industrial compost environment, has attracted attention in the previous decades. It has become an economically viable commodity of plastics industry used for the production of common use products and packaging materials as trays, bottles or films [6,7].

The second biodegradable polymer in the studied polymer blend was polyhydroxybutyrate (PHB). Because PHB is relatively brittle, expensive and sensitive to thermal degradation, it is usually advantageous to use it in polymer blends to promote overall properties instead of producing it in pure form [8]. PHB can be plasticized with dioctyl phthalate, 1,4-cyclohexanedimethanol dibenzoate, tert-butylphenyl phosphate, PEG, triacetyl glycerol, tributyrin, dodecanol, lauric acid, trilaurin and low molecular weight poly (adipate) [9–11].

Both polymers PLA and PHB are biodegradable polyesters and are used in consumer products by several industries due to their biocompatibility and biodegradability. They have comparable thermal and mechanical properties as the properties of some common polymers, which has aroused considerable interest in investigating their physical and processing properties for potential applications [12–14]. PLA and PHB are known to have poor processing properties and are brittle at the room temperature [15]. PLA has better mechanical performance than

PHB while PHB displays better barrier properties [16–18]. Several authors have proposed blending PLA and PHB as a strategy to modify unfavorable characteristics and improve properties of each virgin polymer [19–23].

Previous studies of PLA/PHB blends have shown that the miscibility between the two polymers depends on the molecular weight of the second component [12,24–26]. PHB is miscible with low molecular weight PLA in the melt throughout the composition range, while mixtures of PHB with high molecular weight PLA shows biphasic separation [24,25]. Similarly, the PLA component is miscible with low molecular weight PHB (Mw = 9400) in a melt with a PHB content of up to 50% by weight and is immiscible with high molecular weight PHB and commercial grade bacterial PHB [15,26]. The properties of PLA/PHB mixtures also depend on the composition, chemical or physical crosslinking and processing conditions. Zhang et al. [16] investigated the morphology, structure, crystallization, thermal properties, mechanical properties and biodegradation of PLA/PHB mixtures, which were prepared by melt mixing. The PLA/PHB blend in ratio of components 75/25 showed improved mechanical properties, thermal decomposition temperature and the presence of some interactions. In general, PLA/PHB mixtures exhibit better barrier properties than PLA [17,27], but still relatively low strain at break values (improvements lower than 1%) [19, 22]. To overcome this drawback, the incorporation of plasticizers have been proposed, resulting in a decrease in glass transition temperature (Tg), a better material processability and an improvement in its flexibility [17,19,28,29]. For example, elongation at break values (εb) reported for PLA/PHB (75:25 w/w) blended with different plasticizers are in the range of 6%–15% for poly (ethylene glycol) (PEG) [17], D-limonene [22] and Lapol 108 [19], and 90% for acetyl tributyl citrate (ATBC) [28]. In addition, acetyl tributyl citrate (ATBC) have also proved to be effective in accelerating the disintegration process under composting conditions [28]. The patent EP2710076B1 [30] shows that blending PLA and PHB in a suitable ratio with adding a suitable type of plasticizer improve mechanical properties and even increase flexibility of PLA/PHB blends. The presence of a plasticizer suppresses the degradation induced by thermomechanical stress during processing of studied polymer blend. Yang et al. [31] focused on the use of degraded PHB as a plasticizer for the production of PLA-based polymers by extrusion. The results obtained were very promising because the inoculated PLA with 20% (w/w) of PHB oligomers showed a high ductility and toughness. In addition, the new polymeric composition had an elongation at break 66 times higher than pure PLA. Another way to improve the compatibility of the PLA/PHB blends is to use a compatibilizer. These compatibilizers include glycidyl methacrylate (GMA) [29,32] or poly (vinyl acetate) (PVAc) [33–36]. PLA/PHB blend has various applications; however, some materials should be added to the blends to endow the desired properties.

PLA/PHB blends are biodegradable materials commonly investigated for food packaging applications [22]. One of the potential application fields of these materials is as a film. It has been reported that 25 wt% of PHB produced a reinforcement effect on PLA matrix [16]. Arrieta et al. in different studies [22,37–39] investigated the behavior of PLA/PHB blends with various plasticizers for food packaging applications. They showed that natural terpene D-limonene (LIM) as plasticizer raised the crystallinity of PLA and resulted in flexible films. They also showed that PHB played a reinforcing role in the PLA matrix and hence improved the oxygen barrier properties and surface water resistance. Similar results were reported on the effect of ATBC on the mechanical and disintegration behavior of electrospun fibers of PLA/PHB blends. Electrospun nanofibers of PLA/PHB blends were successfully developed by Nicosia et al. [40] for air filtration and antibacterial applications. The PHB/PLA composite due to its high mechanical strength had been recommended also for medical implantation [41]. PLA blends with a copolymer of PHB named poly (3-hydroxybutyrateco-4-hydroxybutyrate) (P (3HB-co-4HB)) were studied in Refs. [42–44] for packaging applications. The blends were found to be immiscible, but of high

compatibility. The crystallization rate of PLA, the strain at break and biodegradability were improved in the presence of P (3HB-co-4HB). PLA/PHA blends could be helpful compostable materials for long-term agricultural applications, including row covers and landscape fabrics [45]. The blends PLA/PHB for their improved utility properties and improved biodegradability were also investigated for using in additive manufacturing - 3D printing [46,47].

Broniarz et al. [48] proposed that a blend composed of 70 wt%. PLA with 30 wt% PHB could be used as an effective candidate for the gel polymer electrolyte used in Li-ion battery applications since the membrane fabricated from PLA/PHB blend exhibited attractive merits, such as high porosity, high conductivity, and high electrochemical stability.

Since PLA/PHB have gain considerably interesting during the last decade, it is interesting to recycle these widely applied formulations.

However, biodegradable plastics from renewable resources also exhibit number of disadvantages such as brittleness, degradation during processing but also their impossibility of material recycling with commonly used synthetic plastics. For this reason, there is currently very little scientific work on material recycling of biodegradable polymer materials. However, in view of circular economy in terms of environmental protection, it is desirable to explore a possibility of re-using such materials through material recycling.

Various plastic waste management strategies have been studied, ranging from reuse and recycling (Mechanical, Chemical, Feedstock) to thermolysis/recovery processes [49–51]. From the point of view of energy and the environment, the research works [52–55] emphasized that a mechanical recycling strategy is the most appropriate plastic waste management option for relatively clean and homogeneous plastic and bioplastic waste in comparison with landfill or incineration alternatives.

Mechanical recycling allows directly recovery of plastic solid waste for reuse in the production of new plastic products [49,51,53,56], and can use traditional technologies and commonly used processing machines such as conventional extruders and injection moulding machines.

Due to the fact that the process results in different degrees of degradation of the polymer, mechanical recycling is limited by the number of repeated processing cycles [57]. Material recycling has been commonly used for many years in the management of plastic waste resulting from the industrial processing of polymeric materials [58,59]. Also according to European strategy for plastics in circular economy [60] by 2030 all plastic packaging placed on the EU market should be either reusable or able to be recycled in a cost-effective manner and more than half of all plastics waste generated in Europe should be recycled. According to this strategy [60] also innovative materials and alternative feedstock for plastics production should be developed and used where evidence clearly shows that they are more sustainable compared to the non-renewable alternatives. The degradation of the polymer in the extruder is one of the main factors that can adversely affect the material quality of plastics during material recycling. The term deterioration of material quality means processing deterioration, deterioration of mechanical or thermal properties of the material, as well as electrical and optical properties or appearance and aesthetic properties of the material [61,62]. Polymer degradation during processing also reduces the productivity of re-used material due to viscosity differences mixing recycled and virgin polymer to receive applicable products. Degradation is affected by many factors such as shear stress, temperature, humidity, pH, presence of oxygen, UV radiation and presence of other processing additives (for example stabilizers) [63,64]. The growing amount of generated plastic waste, legislative requirements and increased interest of people in environmental protection are the reason to use plastics in the highest number of "living" cycles. Therefore, it is very important to recognize the effect of multiple extrusion of different polymer materials on the final properties of these materials. Several publications have been published on multiple uses of conventional synthetic plastics, such as PP, PE or PVC [65–72], where changes in the final properties of materials based on multiple material extrusion are described. However, until now only few scientific works have been

devoted to describing changes in properties of biodegradable materials from renewable sources during multiple processing of these materials in experimental way [73,74].

PLA is one of the most studied bioplastics related to recyclability. PLA can biodegrade under certain conditions, such as in the presence of oxygen and moisture [75]. Although PLA is biodegradable, which significantly reduces the negative impact of PLA waste on the environment, it is important to recycle the material and investigate changes in the properties of PLA during its multiple processing. Multiple extrusion of PLA up to 10 times was investigated by Żenkiewicz et al. [76] using a twin-screw extruder followed by laboratory injection moulding machine, for preparation of the test samples. The tensile strength values of PLA did not significantly depend on the number of extrusion cycles. Another study [77] on PLA reprocessing (containing 92% L-lactide and 8% D-lactide) showed that only the tensile modulus remains constant with thermomechanical cycles of up to seven injection mouldings. Conversely, stress and tensile stress, modulus, hardness and rheological factors generally show reduced values. The viscosity of PLA decreases significantly (from 3960 to 713 Pa s) after only one injection cycle. The mechanical properties of recycled PLA have become too poor for the industrial use of the polymer.

In Badia work [78], the influence of multiple thermomechanical processing on the structure and properties of the amorphous type of PLA was studied. Due to the multiple processing of amorphous PLA the molecular weight in this case as well and the studied properties of the polymer deteriorate decreased, especially after the 2nd processing transition in the case of injection moulding.

In Agüeo's work [79], it was found that the effect of multiple extrusion of PLA leads mainly to a decrease in the elongation at break and also the impact strength. PLA is sensitive to the hydrolysis of ester bonds, but during extrusion in the first three processing cycles no significant degradation of the material occurs and PLA can be recycled in the three cycles of extrusion. The Rivas article [80] studied the properties of PHB after multiple extrusion (3 cycles of recycling). During reprocessing, the mechanical properties deteriorated significantly, when the tensile strength of the material after triple extrusion reached less than 50% of the original value of the tensile strength.

The mixture of copolymer polyhydroxybutyrate/polyhydroxyvalerate (PHBV) and PLA has been investigated for recycling by extrusion and injection moulding [81]. Compared to the PHBV, the mixture of PHBV and PLA was more stable in thermomechanical degradation where mechanical properties (tensile strength, elongation at break and impact strength) remained more or less stable even after six cycles of reprocessing. Preservation of mechanical properties has revealed the stabilizing effect of PLA in PHBV/PLA blends, which opens up a promising opportunity to expand polyhydroxyalkanoates recycling and applications.

This study describes the effect of multiple extrusion on final mechanical, thermal and optical properties, as well as processing stability of commercial available biodegradable polymer blends under trademark NONOILEN® based on PLA and PHB. NONOILEN® represents modern plastic material fulfilling all ecological requirements based on main circular economy principles. It is polymeric blend which combines various benefits of basic components and eliminate their weaknesses. NONOILEN® consists of PLA, PHB, plasticizers and eventually nucleating agent, antiblocking agent or other additives according to specifics of given applications. Mainly esters of citric acid are applied in role of plasticizers or some oligomeric esters of di- or more carboxylic acids, preferably esters of adipic or citric acid. All these plasticizers can be produced based on renewable materials and they are ecologically safe without any negative effect on human or animal health.

Table 1
Basic properties of NONOILEN® IM 3056–2.

Parameter	Unit	Value
MFI	g/10 min at 2,16 kg, 180 °C	5.8
Density	g/cm^3	1.2
Tensile strength at break	MPa	49.1
Elongation at break	%	2.8

Note: The results assigned to the zero processing cycle and the results at the extrusion time 0 correspond to the results of the virgin polymer mixture NONOILEN® IM 3056–2 (with PLA/PHB ratio = 45/55).

2. Experimental

2.1. Materials

NONOILEN® IM 3056–2 is an injection moulding grade of PLA/PHB based blend produced by Panara Ltd. Slovakia. PLA/PHB ratio in the blend was 45/55 by weight. NONOILEN® IM 3056–2 was used as delivered.

The basic properties of polymer blend NONOILEN® IM 3056–2 are described in Table 1.

2.2. Methods of samples preparation and experiments

2.2.1. Multiple extrusion

Tested biodegradable polymer blend was processed by single-screw extruder Plasticorder Brabender equipped with a screw of 19 mm in diameter, L/D = 25, compression ratio 1:3. Head of extruder was equipped with the circular cross section die nozzle, diameter 2 mm. Temperature profile of the extruder was: 170-190-185-180 °C in direction from hopper to head and speed of screw was 55 min^{-1}. Material retention time in extruder of each cycle was 58 s. The strand cooled by air on belt was taken for evaluating of measured properties from each extrusion cycle. Diameter of strand was 1.8 mm. The final number of testing cycles (extrusions) was 11, and thermomechanical stability, mechanical and thermophysical properties and colorimetric changes were tested after each processing cycle.

2.2.2. Processing (thermomechanical) stability

Thermomechanical stability was measured using the oscillation rheometer RPA 2000 from Alpha Technologies. The timed test was used to determine processing stability of polymer blend according to the method described in the paper [82]. The angle of strain was 60° and frequency was 50 cpm. The time period of all tests in each cycle was 10 min at the testing temperature 180 °C. For the correct evaluation of temperature effect on the rate of polymer degradation based on the decreasing of complex viscosity, the elimination of differences of initial viscosity was done by recalculation of complex viscosity to the values of relative complex viscosity using the following formula:

$$\eta_{rel}^* (t) = \eta^* (t) / \eta_0^* \tag{1}$$

where $\eta^*_{rel}(t)$ is the relative complex viscosity at the time t, $\eta^*(t)$ is the complex viscosity at the time t and η_0^* is initial complex viscosity at the start of test.

2.2.3. Mechanical properties measurement

Mechanical properties were measured by using the prepared strands from each extrusion cycle. The strands had a circular cross-section with a diameter of 2,0 mm. Tensile strength at break (σ_b) and the elongation at break (ε_b) were determined according to ISO 527 standard by the Zwick machine at cross-head speed 1 mm/min in the deformation range of 0–3%. When deformation reaches value 3% of elongation, the cross-head speed increased up to 50 mm/min.

Table 2
Conditions for DSC measurements.

		Ramp	Set temperature (°C)	Time (min)
1.	Conditioning	isothermal	0	1
2.	Heating	10 °C/min.	200	20
3.	Conditioning	isothermal	200	1

2.2.4. Thermophysical properties measurement

The differential scanning calorimetry (DSC) was used for the determination of basic thermophysical properties such as glass transition temperature, crystallization temperature and melting temperature of samples after 0; 2; 4; 6; 8; 10 and 11 cycles were measured. The conditions for DSC measurements are summarized in Table 2.

2.2.5. Measurements of colour changes

Colour of tested samples was measured on prepared strands according to the CIE Lab colour scale relative to the standard illuminant D65 over a white background by the reflection spectrophotometer (Techkon SpectroDens). The aperture diameter of the measuring port was 3 mm. Illuminating and viewing selected configuration of this instrument was CIE diffuse/10° geometry and the CIE 1964 supplementary standard colorimetric observer. Colour difference was calculated using formula [2]:

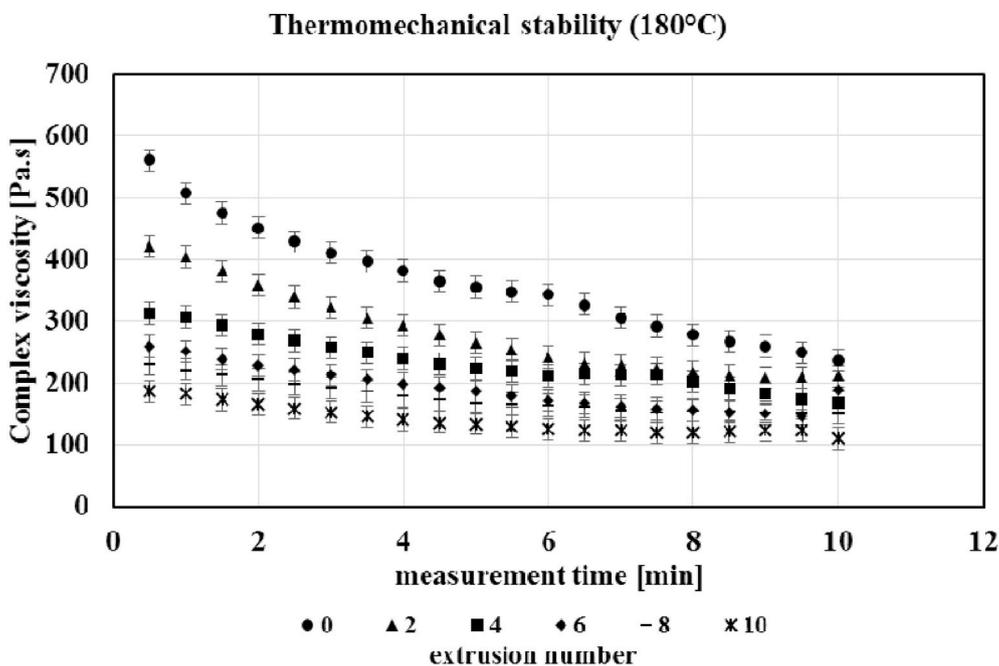$$\Delta E_{a,b}^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \tag{2}$$

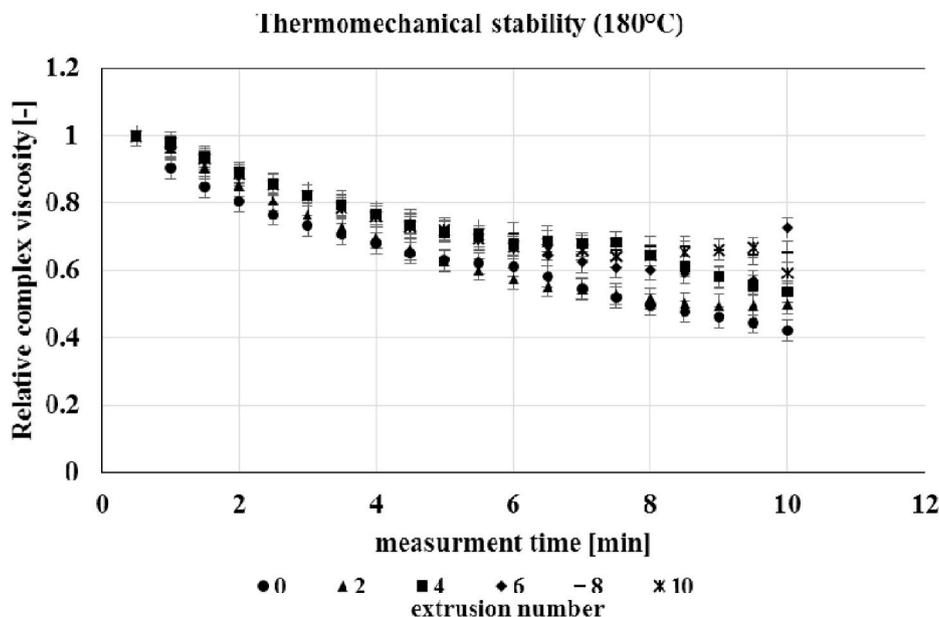Fig. 1. Dependency of complex viscosity on measurement time for each processing cycle.

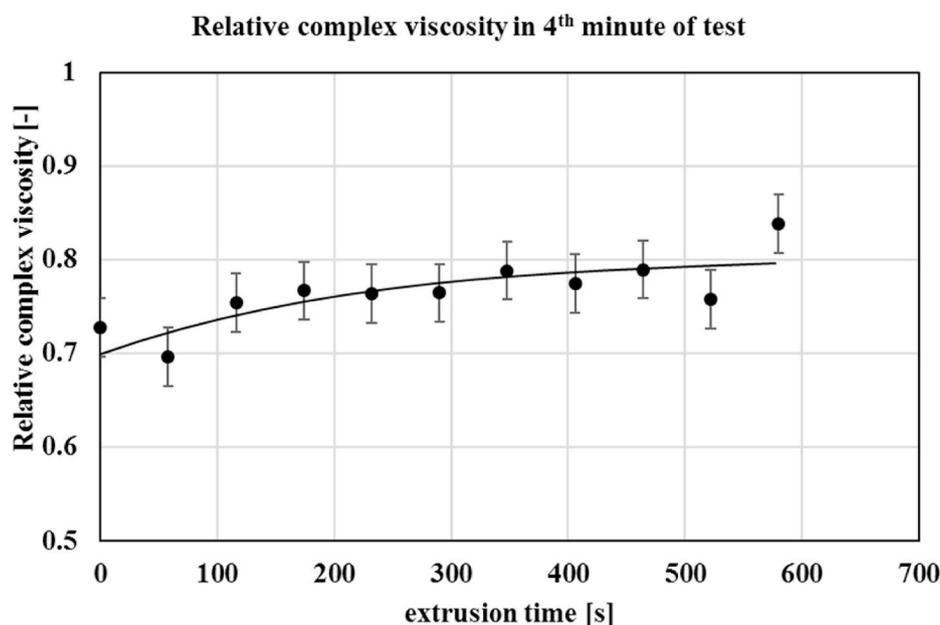Fig. 2. Dependency of relative complex viscosity on measurement time for each processing cycle.

Fig. 3. Dependency of relative complex viscosity on extrusion time of blend at the 4th minute of the test.

2.3. Molecular characteristics

Molar mass of the tested material was determined by gel permeation chromatography. Measurements were performed by the Agilent Technologies 1100 Series instrument equipped with isocratic pump, and an autosampler. PL gel 5 μm mixed C column was tempered to 30 °C with chloroform as the eluent at the flow rate 1 ml/min. Linear polystyrene standards with narrow distribution were used to gain the calibration curve (10 points in calibration). Instrument was equipped with refractive index detector. 5 mg of sample was used for the measurement.

3. Results and discussion

3.1. Processing stability

It is well known that biopolyesters, such as PLA and especially PHB, are very sensitive to degradation during thermomechanical loading, which negatively affects processing properties by rapid viscosity decreasing. This viscosity decrease causes deterioration of the mechanical properties and many other properties of polymeric materials containing these polymers. The effect of multiple extrusion on degradation of polymers is usually described via evaluating of melt flow index (MFI) changes. However, by this method it is not possible to obtain accurate viscosity values of the material at a given time. Also, the MFI measurement of various processing processes does not include material degradation that occurs directly during measurement, alternatively at the filling of the MFI device or at melting of polymeric material before MFI measuring.

For this reason, the oscillation rheometry measurement was chosen for evaluation of processing stability according to the conditions which are described in Ref. [82]. It can be seen from Fig. 1 that due to the multiple treatment of the tested material by extrusion, the absolute values of complex viscosity decrease. There is also a contribution to the decrease in viscosity due to the test time during which the sample is subjected to thermomechanical stress in the oscillating field of the rheometer. Since all factors affecting viscosity are constant during the test, it can be assumed that the decrease in complex viscosity is due to the decrease in molar mass, indicating material degradation. To compare the rate of degradation of the material based on a different number of processing cycles in the extruder, the parameter of relative

complex viscosity was introduced according to equation [1]. This eliminates viscosity differences at the beginning of the test. Fig. 2 shows the dependence of relative complex viscosity on the retention time of the sample in the rheometer under oscillation stress as a function of the number of processing cycles. As can be seen from Figs. 1 and 2, the absolute values of viscosity logically decrease with number of processing cycles. Relative scale of complex viscosity shows that the rate of degradation slowly decreases with the number of processing cycles. It shows that the main degradation process is significant mainly in the first cycles. On the other hand, the latest extrusion cycle shows a small increase in relative viscosity during the oscillation test similarly to the absolute values of viscosity in Fig. 1 (0, 2 and 4 cycles). It can be explained by possible reaction between blend components. This phenomenon was also observed in the article [81].

The change in degradation rate after multiple processing of Nonoilen in a single screw extruder is better visible if the relative complex viscosity is correlated to the retention time in the extruder. In Fig. 3 the relative complex viscosity in the 4th minute of the timed test is shown as a dependency on total processing time in the extruder. It can be seen that the rate of degradation of the material exhibits only marginal changes which are covered by experimental error. It means that the rate of degradation practically does not depend on the time of thermomechanical loading during extrusion in a single screw. All samples after 4 min in the oscillating rheometer reach approximately from 70% to 80% of their initial viscosity.

It can be stated that the formation of a polymer blend of the PLA/PHB type had in our case a very positive effect on the processing stability of biodegradable polymer blends in comparison with the PLA or PHB polymers themselves, where already at the 3rd (PHB) resp. 5th (PLA) during the processing transition there is such a large decrease in viscosity due to degradation that the material cannot be subsequently processed [78–80]. The positive effect of blending PLA/PHAs on processing stability was also demonstrated in the article [81], where during 6 processing passes the decrease in viscosity compared to the non-recycled blend was minimal.

3.2. Molecular characteristics

Molecular weight as well as distribution of molecular weight were evaluated based on GPC measurements. The distribution curves for 0, 3,
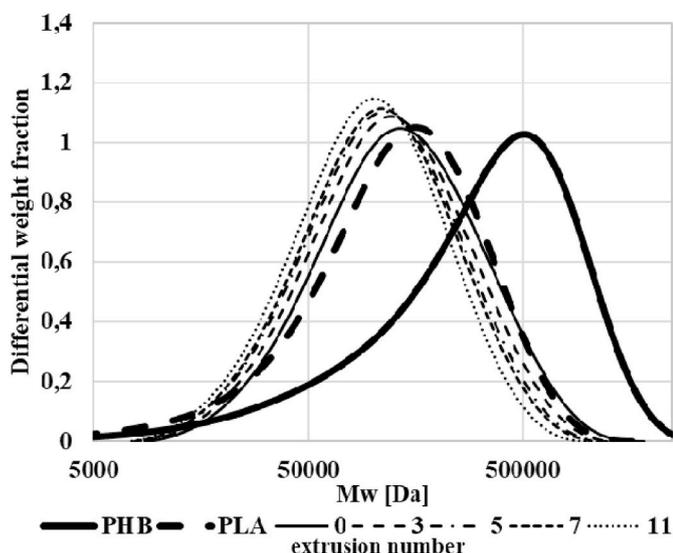
Fig. 4. Distribution of molar mass in dependency on various processing passes.

5, 7 and 11 passing through the extruder are shown in Fig. 4. It is interesting that Nonoilen with ratio of PLA/PHB 45/55 exhibits smooth distribution curve and does not exhibit multiple maxima corresponding to original polymers. GPC measurements of PLA and PHB were realised with the same polymers which were used for Nonoilen blend production. Both PLA and PHB were kindly delivered by Panara company. With the increasing of the pass number the maximum of distribution curves is shifted to lower molecular weights due to a partial degradation of components. Figs. 5 and 6 show very good correlation between extrusion time, molecular weight and complex viscosity. It means, that oscillation rheometry method which was used for processing degradation study reflects changes in molecular weight very well.

3.3. Colour changes

Degradation process during processing of polymers usually also causes changes in colour. The colour changes as results of multiple processing of Nonoilen were evaluated. The dependence of ΔE parameter on cumulative processing time which represents the total chromatic declination from the white standard is shown in Fig. 7 and the dependency of L coordinate on the cumulative extrusion time is shown in Fig. 8. It is clearly seen that the degradation of the tested grade of Nonoilen directly affects the colour difference (ΔE) when ΔE increases with the extrusion time. The decreasing of the L coordinate confirms that the samples after longer extrusion time become darker. Fig. 9 shows the colour change of the material. It is seen that the material darkens with a higher extrusion number. The results of identifying the colour changes during the processing of Nonoilen PLA/PHB biodegradable and bio-based blend simultaneously with the previous results show that also colour changes very well reflect degradation process and they are in very good correlation with viscosity and molecular mass of the tested polymeric material.

Colour changes were also investigated during multiple processing of amorphous type of PLA [79], where also due to multiple processing there is a decrease in lightness and an increase in colour difference of the tested samples.

3.4. Thermophysical properties

Thermal properties were measured and evaluated using DSC measurements – Fig. 10. Based on evaluation of dependency of the thermal properties on extrusion time it can be stated that the extrusion time has a
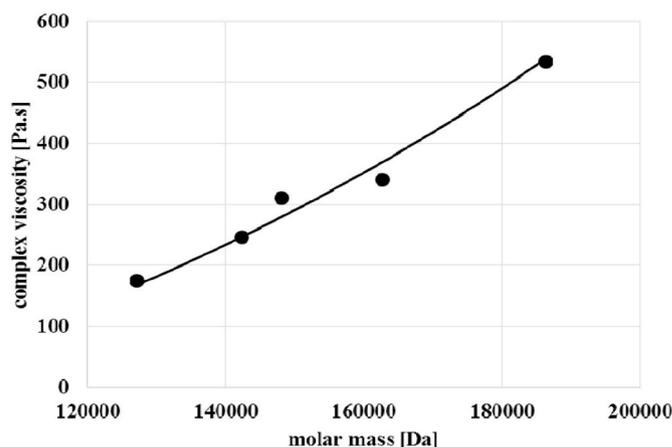

Fig. 6. Dependency of complex viscosity on the 4th minute of oscillation test on initial molecular weight of the tested sample.
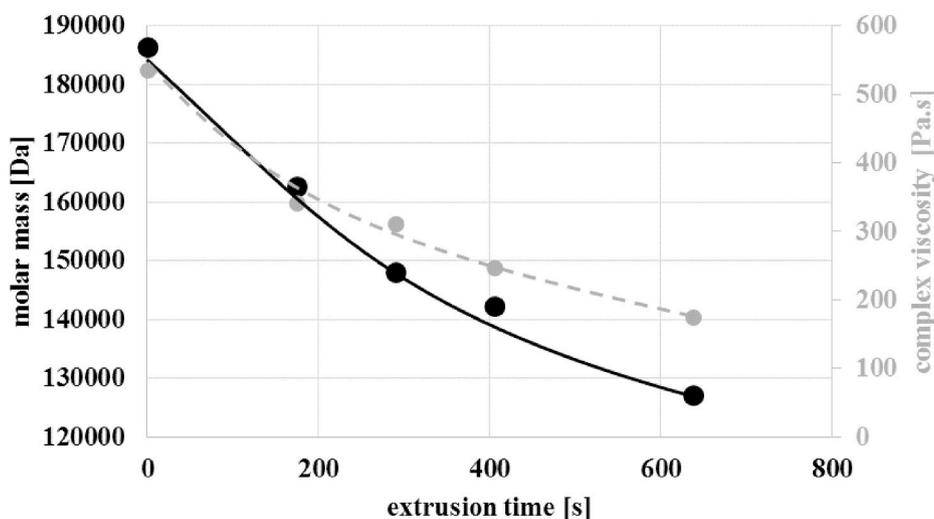

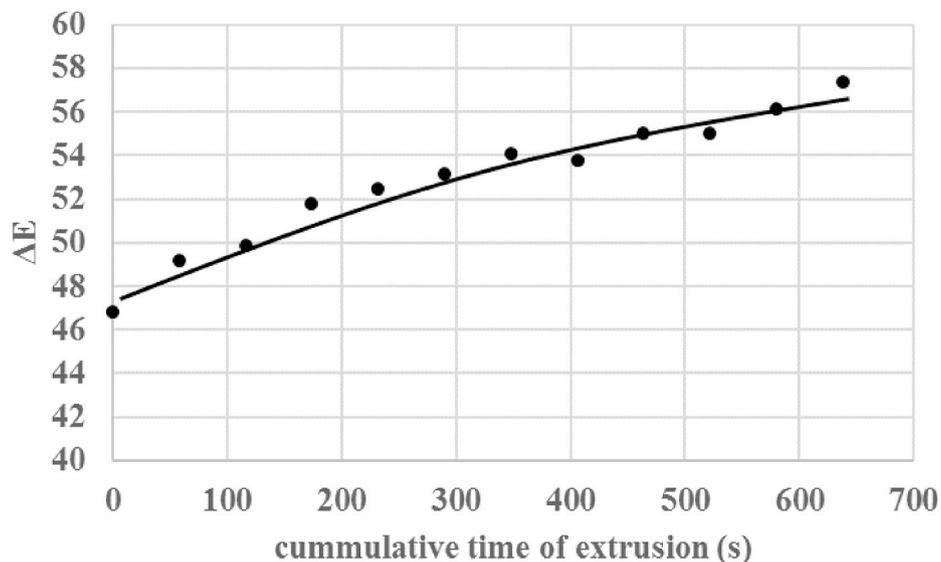**Fig. 5.** Dependency of molar mass and complex viscosity on extrusion time of material.

Fig. 7. Dependency of colour change on complex viscosity of the studied blend.
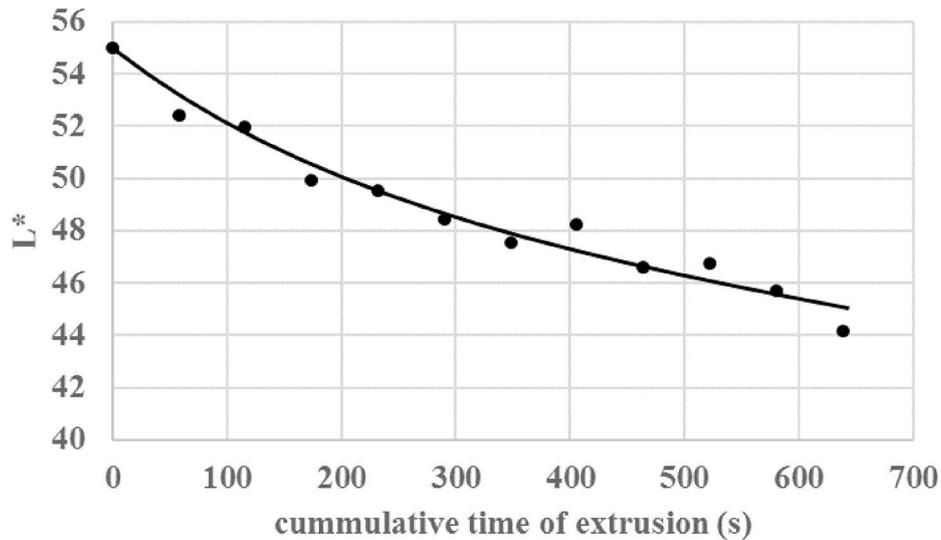

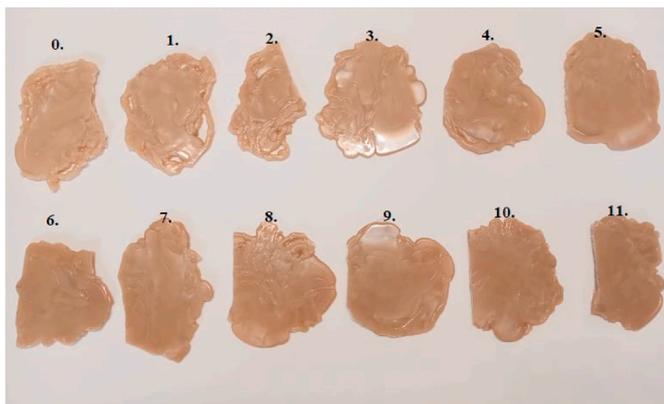Fig. 8. Dependency of lightness on time of extrusion of the studied blend.

Fig. 9. Colour changes of material after different processing cycles (0.-11.).
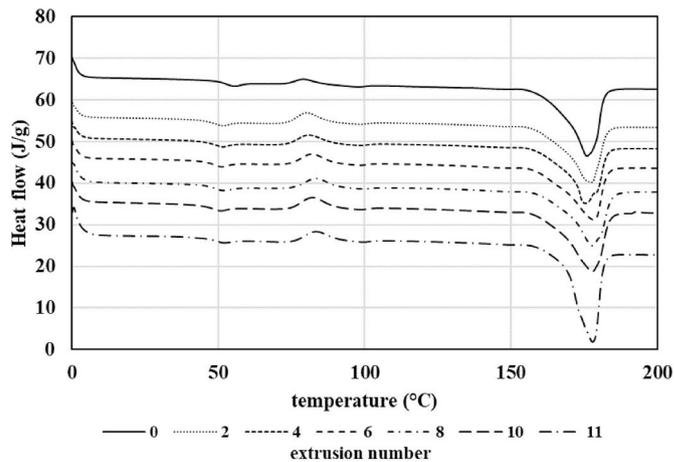

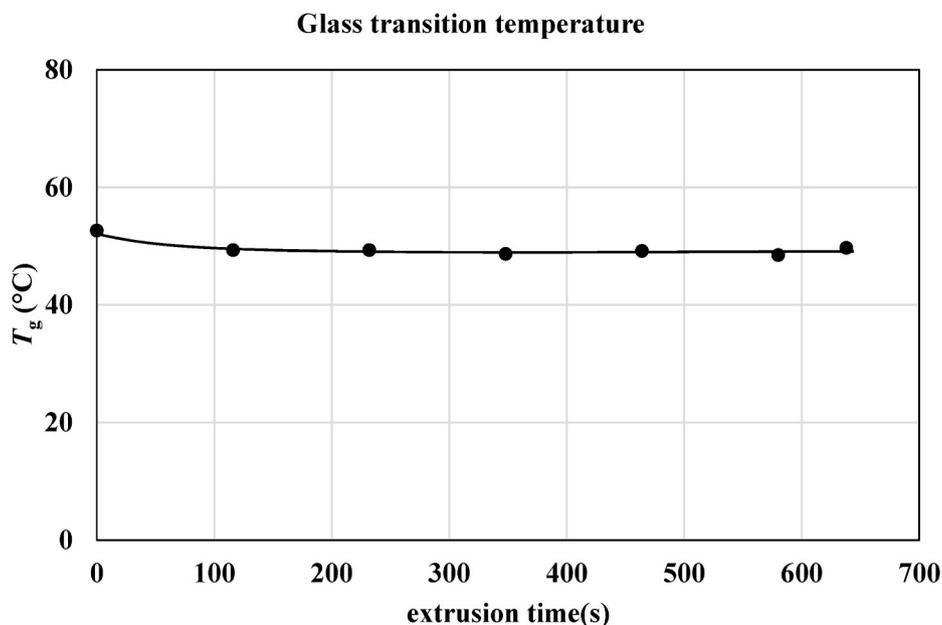Fig. 10. DSC thermograms of each processing cycle.

Glass transition temperature

Fig. 11. Dependency of glass transition temperature on extrusion time.
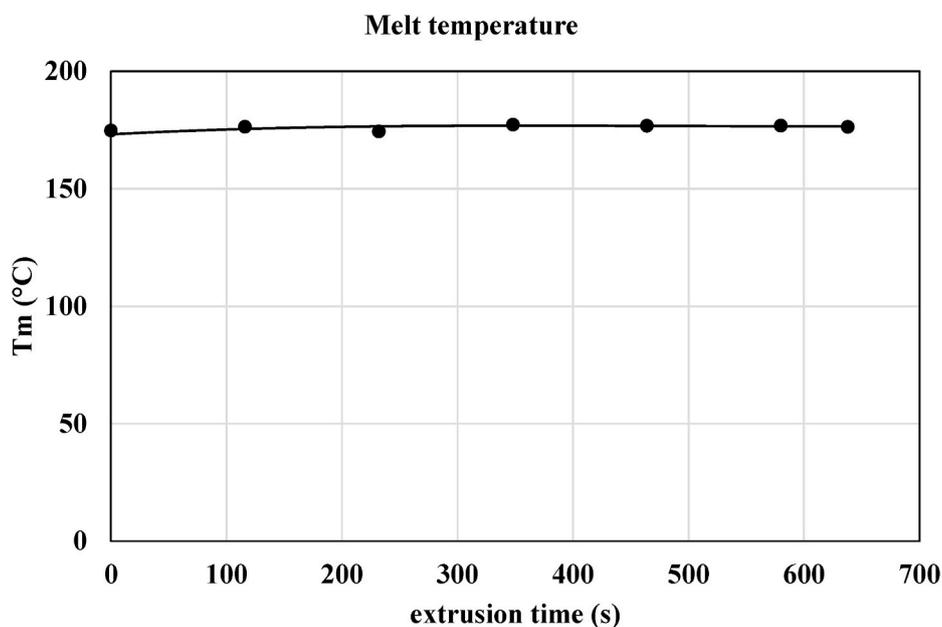
Melt temperature

Fig. 12. Dependency of melt temperature on extrusion time.

minimal influence on thermal properties of the material as the difference between glass transition temperature of the individual materials after multiple processing does not exceed 3 °C. The dependency of glass transition temperature on extrusion time is visible in Fig. 11, where the material without any processing cycle has the highest value of T_g (52.5 °C). After processing the glass transition, the temperature of the material decreases to the value about 49.5 °C. This result also corresponds to scientific works [78,79,81], where with multiple processing of the PLA itself resp. Of the PLA/PHBV polymer blend, there is only a minimal effect on the Tg of the tested material. Also, the melting point of the crystallites and the melting enthalpy of the crystallites are practically without changes in dependency on the extrusion time (Figs. 12 and 13). In this case, it should be noted that in other scientific works that

have dealt with multiple thermomechanical processing of PLA and PLA/PHAs [77–79,81], the enthalpy of crystallization and enthalpy of melting of crystallites increase due to multiple processing and thus the crystallinity of the polymer or polymer blend is increasing. We suppose that this phenomenon is caused by a significant decrease in viscosity, which the authors report, and thus by better mobility of polymer macromolecules compared to the polymer blends studied by us. Interestingly, the studied biodegradable polymer blend shows only one crystallite melting peak. From DSC results, it can be predicted that, despite partial degradation of the material during multiple processing, there is no significant change in thermal properties and no significant change in crystallinity of the material. This may indicate that due to the multiple processing, the barrier properties and strength characteristics
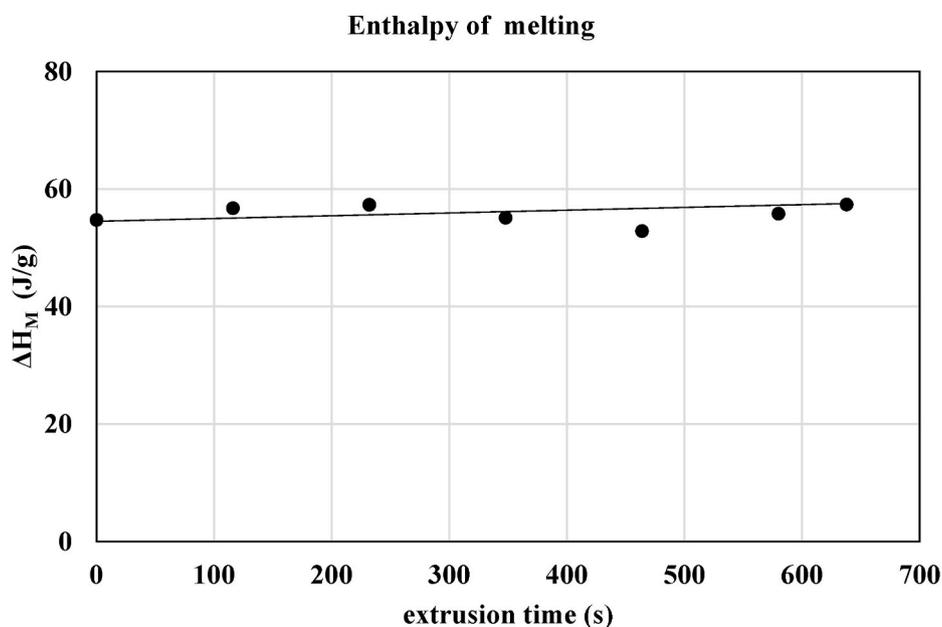
Enthalpy of melting

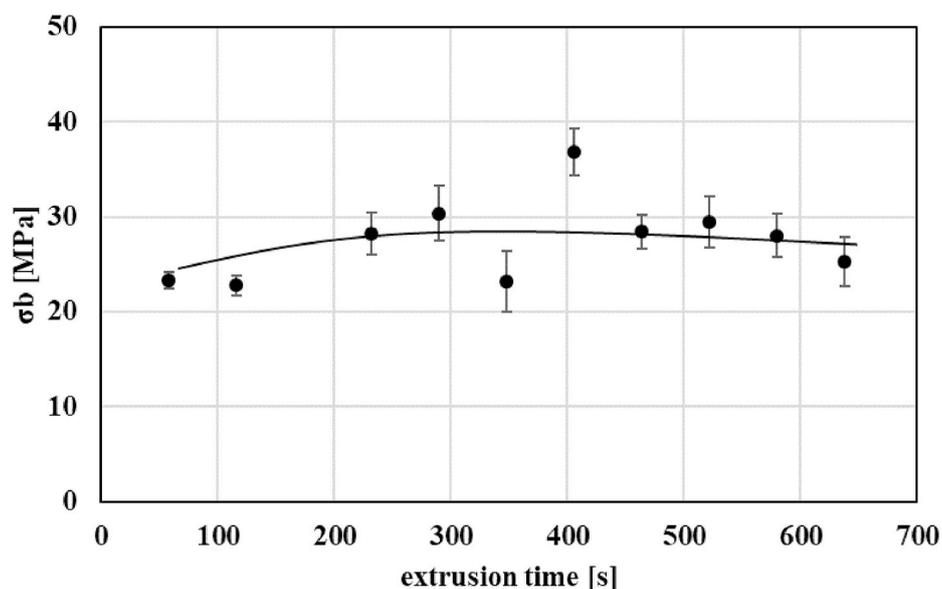Fig. 13. Dependency of melting enthalpy on extrusion time.

Fig. 14. The dependency of strength at break on extrusion time of the tested blend.

of the test material will not deteriorate.

3.5. Mechanical properties

Evaluation of tensile strength and elongation at break in dependency on cumulative extrusion time shows, that tensile strength varied between 23 and 35 MPA approx. (Fig. 14). Elongation at break falls down only in the first stages of extrusion time and after 200 s no changes can be observed on graph presented in Fig. 15. During multiple extrusion process, the tested blend exhibited relatively stable values of tensile strength of break in the range from 23 to 35 MPa. Decreasing of the relative elongation at break values can be connected also with material degradation and with reduction of polymer chains length.

Even in this case, it can be stated that the PLA/PHB mixture is more suitable for multiple processing compared to the PLA or PHB polymers themselves, because in the case of PHB [80] the tensile strength decreases by more than 50% after only three processing cycles compared to the initial value and in the case of PLA after the 7th processing transition, the values of tensile strength decrease from the initial value of 65 MPa to the value of 25 MPa [77]. However, it should be emphasized that in this case it was a multiple injection of material, where higher shear rate affects on the material. With multiple extrusion of PLA, the values of strain at break decrease by about 10% from the initial strain at break values (from 55 MPa to 50 MPa) after the 6th processing cycle [79]. In our case, the decrease in strength did not occur even after the 11th processing cycle.
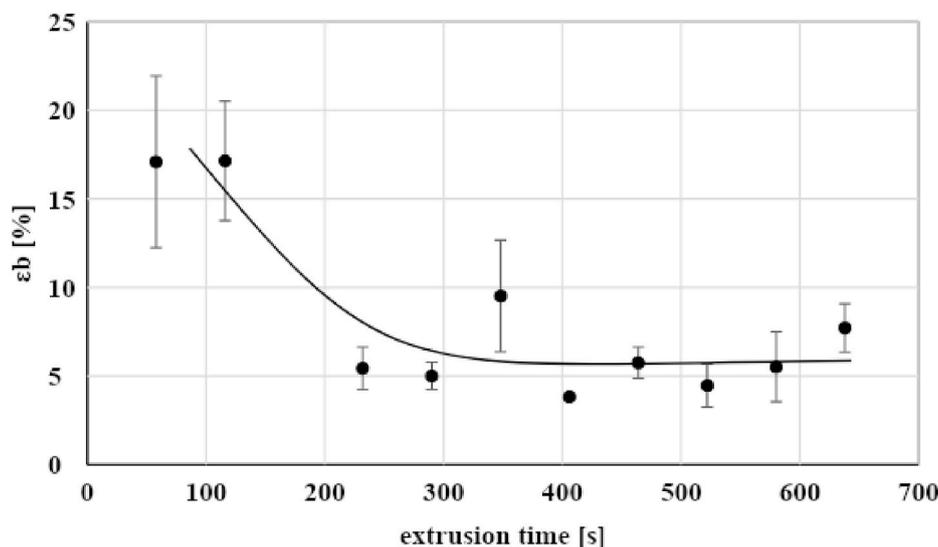
Fig. 15. Dependency of elongation at break on extrusion time of the tested blend.

4. Conclusion

Influence of multiple extrusion as a model for material recycling of biodegradable PLA/PHB blend on basic blend properties was studied. Increased extrusion (processing) time causes reducing of viscosity of the tested blend. On the other hand, rate of degradation did not increase due to longer extrusion time. Decreasing of molecular weight was confirmed using GPC. The average molecular weight as well as polydispersity index decrease as an effect of multiple reprocessing of the blend. Degradation of the material was also reflected in the change of material colour, which was determined by the CIE Lab colour space coordinates (ΔE, L *). The degree of degradation of the tested material can be determined with relatively high accuracy after creating a colour space/complex viscosity curve using this method. We consider a positive result that the multiple processing and subsequent degradation of the tested material did not negatively affect thermal properties of the blend. Increased diffusion of the plasticizer from the polymer matrix did not appear and there was not observed increasing glass transition temperature or crystallite melting point. Interestingly, the mixture exhibited the character of a miscible mixture at a molecular level, assuming from the presence of only one melting peak of the crystallites. Also, multiple processing did not affect negatively the strength characteristics of the blend, even though there was a slight increase in tear strength. Conversely, the flexibility of the material decreased by multiple processing, but in general, this parameter in absolute values was close to the initial values of the original blend. To the decrease of elongation at break occurs just after 2nd processing cycle. It follows that until the 2nd processing cycle, the material retains its original user properties, while until this time no changes were observed in the processing of the polymeric material, which would be caused by a decrease in viscosity due to degradation. Despite the decrease in elongation at break, it can be stated that the studied mixtures retained similar values of mechanical properties as the non-recycled PLA/PHA polymer blends studied in the articles [16,18,83, 84]. Recycled Nonoilen blends could be used in the applications that do not require high material flexibility.

From the results shown in this work, it can be stated that compared to PLA and PHB polymers themselves, the PLA/PHB blend has better resistance against degradation at multiple thermomechanical stress, which has a positive effect on the processing process and mechanical properties of the tested material. It should be emphasized that in the case of the tested polymer blend PLA/PHB we were able to perform 11 processing passes without significant changes of studied properties, especially of rheological and mechanical properties of the material, unlike PHB itself, where the authors were able to perform 3 processing passes [80] and in the case of PLA, where the authors prepared a maximum of 10 processing passes [77].

It can be concluded that the biodegradable polymer blend of the PLA/PHB type is suitable for material recycling.

CRediT authorship contribution statement

Roderik Plavec: Conceptualization, Writing - original draft, Methodology. **Slávka Hlaváčiková:** Investigation, Writing - review & editing. **Leona Omaníková:** Methodology, Investigation. **Jozef Feranc:** Resources. **Zuzana Vanovčanová:** Visualization. **Katarína Tomanová:** Investigation. **Ján Bočkaj:** Resources. **Ján Kruželák:** Formal analysis. **Elena Medlenová:** Resources. **Ivana Gálisová:** Project administration. **Lucia Danišová:** Investigation. **Radek Přikryl:** Supervision. **Silvestr Figalla:** Validation. **Veronika Melčová:** Investigation. **Pavel Alexy:** Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

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