

# APPLICATIVE AND RHEOLOGICAL PROPERTIES OF PLA MASTERBATCHES WITH CONTENT OF PLASTICIZER AND BIOPLASTICIZER

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**Abstract:** Synthetic fibres prepared from standard types of polymers such as PP, PA and PET are no longer sufficient to cover all user requirements, therefore standard types of polymers are mixed and modified with various additives such as pigments, plasticizers, dispersants etc., and at the same time new types of polymers are being sought for fibres production. The effort of fibre producers and their processors is to meet the needs of users as much as possible. As there is currently a global problem with waste plastics, various solutions are being sought, either by recycling synthetic plastics or by looking for new biodegradable polymers. In recent years, much attention has been focused on polylactic acid (polylactide), which is biodegradable under certain conditions. In the present work, masterbatches prepared from two types of polylactic acid with 15% additive content will be studied. Polylactic acid is very brittle, which makes a problem in the preparation of fibres, so this article is focused on evaluating the PLA masterbatches containing plasticizers. In generally, plasticizers help to reduce the brittleness and increase the elasticity of the fibres. The applicative and rheological properties of the prepared PLA masterbatches were studied. The flow properties of masterbatches containing 15% non-biodegradable plasticizer with masterbatches containing 15% biodegradable plasticizer were compared.

**Keywords:** PLA masterbatches, applicative properties, rheological properties, plasticizer, bioplasticizer.

## 1 INTRODUCTION

As a result of the corona crisis, global economic growth in 2020 recorded the slowest pace since the financial crisis ten years ago, including the textile industry. The total volume of fibres in 2020 was 120 million tons, of which 74 million tons were synthetic fibres, including staple fibres. Synthetic fibres achieved 5% growth due to the robust expansion of polyester fibres and staple fibres, while nylon rose slightly and both acrylic and polypropylene fibres weakened [1]. The pandemic led to a sudden surge in global demand for personal protective equipment, such as masks, gloves, gowns and bottled hand sanitizer resulting in increased solid polymer waste accumulation. The use of durable polymers is therefore a disadvantage [2-4]. The 21<sup>st</sup> century is focused on materials that will decompose in the natural environment, in soil or compost [5]. PLA offers unique properties of biodegradability, biocompatibility, thermoplastic processability and ecological safety [6, 7]. Plasticizers or dispersants are additives which increase the plasticity or decrease the viscosity of a material. They are the substances which are added in order to alter their physical properties. They decrease the attraction between polymer chains to make them more flexible [8, 9].

Permanent functional modifications of chemical fibres are most often ensured by adding a functional additive to the polymer mass of the fibre through the preparation of a masterbatch which is added to the base polymer in the spinning process. The masterbatch must have suitable rheological and applicative properties (it must not reduce the technological stability of the fibre preparation process). The masterbatch added in a defined ratio to the main polymer stream is melted, homogenized and spun into fibres together with the base polymer [10].

The paper presents the results of a study of the influence of two types of plasticizers and two types of PLA polymers on the applicative and rheological properties of prepared masterbatches. Four 15% masterbatches were prepared by mutual combination. The flow (applicative and rheological) properties mentioned above of masterbatches containing 15% non-biodegradable plasticizer with masterbatches containing 15% biodegradable plasticizer were compared. The obtained experimental results were evaluated from the point of view of the suitability of the flow properties prepared masterbatches for modified PLA fibre preparation.

## 2 EXPERIMENTAL AND METHODS

### 2.1 Materials

**Polymers:** polylactic acids: **PLA1** with MFI=24.6 g/10 min (210°C/2.16 kg) and **PLA2** with MFI=8.9 g/10 min (210°C/2.16 kg), both produced by Total Corbion PLA B.V.

**Additives:** plasticizer **PL** with MFI=6.0 g/10 min (210°C/2.16 kg) and bioplasticizer **BioPL** with MFI=8.9 g/10 min (210°C/2.16 kg) were used.

### 2.2 Preparation of PLA masterbatches

Before preparation of masterbatches the premixes have been prepared. The premixes consisted of a mutual combination of two PLA carriers (PLA1 and PLA2) and two types of additives (PL and bioPL). Both the polymers and the additives were milled and dried at 85°C for 4 hours before preparing the premixes.

PLA masterbatches were prepared on a laboratory Werner-Pfleiderer ZDSK 28 twin-screw extruder with vacuum zone and screw diameter of 28 mm. The preparation process of masterbatches had been carried out at a constant screws rotation speed 270 min<sup>-1</sup> and constant extrusion temperature of 210°C. The output was four 15% masterbatches (Table 1).

**Table 1** The masterbatches composition

Masterbatch No.	Name of masterbatch	Masterbatches composition [wt.%]		
		PLA carrier	PL	bioPL
1	PLA1/PL	PLA1	15	-
2	PLA1/bioPL	PLA1	-	15
3	PLA2/PL	PLA2	15	-
4	PLA2/bioPL	PLA2	-	15

### 2.3 Methods used

#### Applicative properties

The melt mass flow index (*MFI*) of masterbatches was evaluated using a Dynisco Kayness capillary rheo-viscometer according to Standard STN EN ISO 1133 Plastics: Determination of melt mass flow index and melt volume flow index of thermoplastic melts.

The filter index (*F*) is given in MPa/kg and represents the value of the fictitious pressure that would be achieved when filtering a melt of a masterbatch containing 1 kg of active ingredient through a system of precisely defined sieves. In our case, the methodology utilizes an experimental mixture of a PLA masterbatch and a basic testing polymer (polypropylene) in an exact concentration to check the dispersability of the plasticizer in the PLA masterbatch. PP polymer is used due to its low moisture content. The filter index of masterbatches was determined using a filtration single-screw extruder with a screw diameter of 25 mm and density of the filtration sieve

with the smallest holes of 15 600 per cm<sup>2</sup>. The filterability of the dispersion (filter index *F*) was then expressed as ratio of an increment of the pressure  $\Delta p$  [MPa] on the filter to a weight unit of the filtrate *m* [kg] at the definite filtration conditions when:

$$F = \left(\frac{\Delta p}{m}\right) \cdot \left(\frac{100}{c}\right) \quad (1)$$

where: *c* is pigment concentration in mixture.

#### Rheological properties

The rheology of 15% masterbatches of polymers PLA1 and PLA2 was tested on a Göttfert RG20 capillary rheometer by measuring the melt mass flow through the capillary with  $L/d = 30/1$  (*L* - capillary length and *d* - capillary diameter in mm) as a function of varying pressure. It was operated in the temperature regime of 190°C and 210°C. The samples were dried at 80°C for 3 hours before measurement. According to Equations 2 and 3, the shear rate *D* [s<sup>-1</sup>] and the shear stress  $\tau$  [Pa] were calculated, where *Q* [mm<sup>3</sup>.s<sup>-1</sup>] is volume flow, *R* [mm] is capillary radius,  $\Delta P$  [Pa] - pressure change, *L* [mm] - capillary length.

$$D = \frac{4Q}{\pi R^3} \quad (2)$$

$$\tau = \frac{R\Delta P}{2L} \quad (3)$$

These equations are applicable to materials that are called Newtonian fluids from a rheological point of view. From the calculated dependences of the shear stress from the shear rate, a seeming flow curves (without correction) were constructed.

Rabinowitsch correction was used to construct a true flow curve that takes into account the non-Newtonian flow pattern at the capillary wall, and the relationship for calculating the shear rate is transformed to:

$$D_{sk} = \frac{3n+1}{4n} \frac{4Q}{\pi R^3} \quad (4)$$

where:  $D_{sk}$  - the real shear rate, *n* - the flow behavior index or index of the deviation flow, *Q* - volume flow, *R* - capillary radius.

From the Ostwald de Waele law (5) for both seeming and real shear rate the flow consistency *K* [Pa.s] was calculated, which expresses the fluidity of the material (a high *K* value means high viscosity) and the non-Newtonian flow index *n* of polymer melts (masterbatches).

$$\tau = K \cdot D^n \quad (5)$$

## 3 RESULTS AND DISCUSSION

#### Applicative properties of PLA masterbatches

Applicative properties give us the initial information about masterbatches. These include the flow characteristics of masterbatches - melt flow index and reciprocal value to the *MFI* - the viscosity,

as well as the filterability value of masterbatches, which informs about their quality. Results of the evaluation of the applicative properties of prepared PLA masterbatches with additives PL and bioPL are presented in Table 2.

By comparing the applicative properties of the masterbatches ( $MFI$ ;  $\eta$ ;  $F$ ) and the types of polymers used, it was found that masterbatches 1 and 2 have higher flow indices and lower coefficients of variation than masterbatches 3 and 4. This difference is due to different PLA matrix types (Table 2). The lower coefficients of variation of the masterbatches melts prepared on the PLA1 matrix demonstrate a more uniform flow through the capillary than the melts of the masterbatches prepared on the PLA2 matrix.

A comparison of the effect of plasticizers on the applicative properties showed a slight diluting effect of the PL plasticizer in both types of PLA matrix used. The plasticizer bioPL does not affect the  $MFI$  of the PLA1 matrix. The increase  $MFI$  of masterbatches 3 and 4 prepared on the PLA2 polymer matrix is due to the degradation of PLA2 during the melt-kneading process. Masterbatches prepared on a PLA1 matrix do not show this phenomenon. Comparison of  $CV_{MFI}$  and  $MFI$  of masterbatches 2 and 4 with bioPL content revealed degradation of PLA2, demonstrating a significant increase in  $CV_{MFI}$  from 8.7% (masterbatch 2) to 21.7% (masterbatch 4), as well as a 46% increase in  $MFI$  of masterbatch 4 over the base polymer PLA2 (Table 2).

A viscosity in the range of 400-900 Pa.s is desirable for the spinning process and is closely related to the desired mechanical properties of the fibres. The viscosity interval of the evaluated masterbatches corresponds to a flow index of 12.5 ÷ 27 g/10 min measured masterbatches.

The filterability of masterbatches is one of the most important properties of masterbatches, because it shows the degree of the additive dispersion in the matrix, what has the effect on the technological stability of the fibres preparation process. Masterbatches 3 and 4 containing PLA2 have low filter index (91 and 35 MPa/kg) indicating a high

degree of the additive dispersion in the PLA matrix without the formation of larger agglomerates. From the point of view of filterability, the masterbatches can be used for the preparation of silk types of fibres with low fineness. Masterbatches 1 and 2 containing PLA1 have higher filter index and therefore meet the requirements for the preparation of fibres with higher finenesses - cotton and wool types. Filter index of studied masterbatches in the range of 35-185 MPa/kg is suitable for the preparation of fibres for research purposes.

It follows from the above that prepared PLA1 masterbatches with suitable applicative properties will not have a negative impact on the technological stability of the fibre preparation process. In PLA2 masterbatches, degradation of the PLA2 matrix can have a negative effect on fibre formation.

#### Rheological properties of PLA masterbatches

The rheological behavior of the melts of PLA masterbatches containing additives PL and bioPL were investigated in order to find the processing conditions in the spinning process. For PLA polymers the manufacturers recommend the processing temperatures of 190°C and 210°C, therefore these temperatures were used to take measure the rheological properties of the masterbatches.

From the measured and calculated values, the non-Newtonian flow index  $n$  (flow behavior index) and the flow consistency  $K$  of the PLA melts of the masterbatches were determined (Table 3). The results showed that masterbatches 1 and 3 containing plasticizer have higher values of flow behavior index (their behavior is closer to behavior of Newtonian fluids) and lower flow consistency (lower viscosities) compared to masterbatches 2 and 4 containing bioplasticizer. All of the above indicates their better processability in fibres preparation.

After editing by Rabinowitsch correction (RC), the flow consistency  $K$  decreased significantly at 190°C (most at masterbatch 4 - PLA2/bioPL from 63 631 to 19 864 Pa.s), at 210°C the decrease of the  $K$  was not so dramatic (at masterbatch 4 from 7 483 to 6 637 Pa.s).

**Table 2** Applicative properties: melt mass flow index ( $MFI$ ), viscosity ( $\eta$ ) and their associated coefficients of variation ( $CV_x$ ) and filter index ( $F$ ) of prepared PLA masterbatches

Masterbatch No.	Name of masterbatch	$MFI^a$ [g/10 min]	$CV_{MFI}$ [%]	$\eta^a$ [Pa.s]	$CV_\eta$ [%]	$F$ [MPa.kg <sup>-1</sup> ]
-	PLA1	24.6	5.1	469	5.2	-
1	PLA1/PL	26.5	9.1	437.3	9.7	185
2	PLA1/bioPL	24.6	8.7	470.4	8.3	107
-	PLA2	8.9	6.6	1 295.1	6.6	-
3	PLA2/PL	16.4	18.0	719.6	20.8	91
4	PLA2/bioPL	13.0	21.7	887.9	24.8	35

<sup>a)</sup> 210°C/2.16 kg ( $\tau = 19500$  Pa), masterbatches were dried 2 h/70°C

**Table 3** Regression parameters: the flow behavior index ( $n$ ) and the flow consistency ( $K$ ) from power model for melts of PLA masterbatches of additives PL and bioPL on polymer carriers PLA1 and PLA2, calculated without and with Rabinowitsch correction (RC)

Masterbatch No.	Name of masterbatches	190°C				210°C			
		without RC		with RC		without RC		with RC	
		K [Pa.s]	n	K [Pa.s]	n	K [Pa.s]	n	K [Pa.s]	n
1	PLA1/PL	15 127	0.386	13 293	0.386	1 474	0.586	1 340	0.586
2	PLA1/bioPL	42 915	0.260	19 553	0.334	4 827	0.486	4 308	0.486
3	PLA2/PL	45 891	0.264	19 698	0.345	3 257	0.518	2 921	0.518
4	PLA2/bioPL	63 631	0.226	19 864	0.341	7 483	0.450	6 637	0.450

The flow behavior index did not change at 210°C, which means that the non-Newtonian character of the flow at the capillary wall did not change. When calculating the Rabinowitsch correction at 190°C,  $n$  increased for all premixes except premix 1, which means that the true melt flow of these premixes on the capillary wall is closer to the flow of Newtonian fluids and less dependent on shear rates than their apparent melt flow - without RC (Table 3).

PLA masterbatches of PL and bioPL additives are pseudoplastic fluids, it means with increasing shear rate the shear stress increases (Figures 1 and 2) and the viscosity (flow consistency) decreases (Figure 3). The pseudoplastic character of masterbatches is also proved by the flow behavior index, the value of which is lower than one (Table 3). Lower values  $n$  indicates a higher dependence of the shear stress on the shear rate at temperature 190°C than at temperature 210°C in the case of the evaluated masterbatches.

From the flow curves without Rabinowitsch correction at 190°C it can be seen that at a shear rate of about 1080 s<sup>-1</sup> the flow curves of masterbatches 2, 3 and 4 intersect and the shear stress of the evaluated masterbatches at this point is the same (Figure 1a).

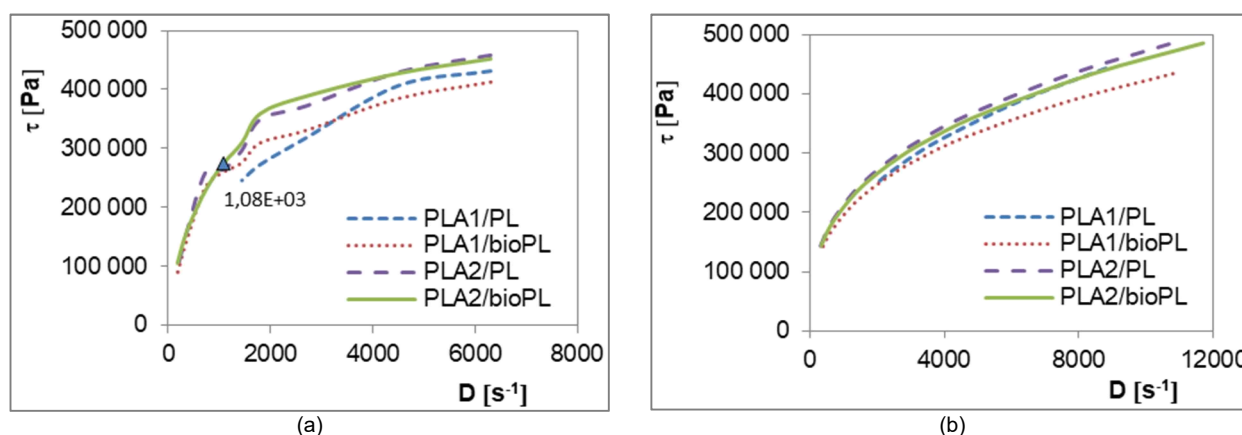
The masterbatches from PLA2 (3 and 4) have higher shear stresses compared to the masterbatches from PLA1, especially in the range of shear rates 2 000-

3 000 s<sup>-1</sup>. At high shear rates above 4 000 s<sup>-1</sup>, PLA2 masterbatches have practically the same running independent of the plasticizer used.

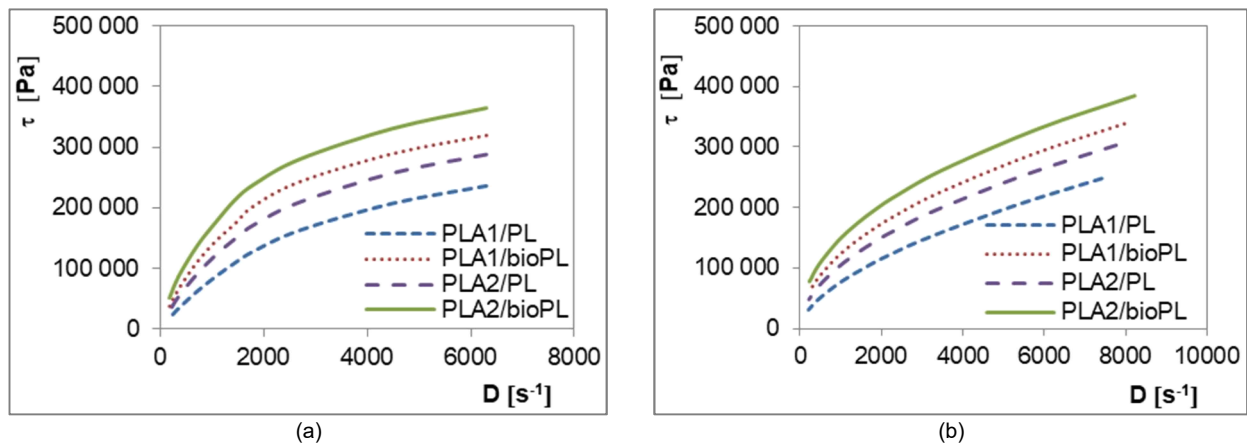
The flow curves of PLA 1 masterbatches intersect at a shear rate of about 3 000 s<sup>-1</sup>. With an increase in shear rates above 3 000 s<sup>-1</sup>, the shear stress of masterbatch PLA1/bioPL was decreased and other hand the shear stress of masterbatch PLA1/PL was increases (Figure 1a). Lower shear stresses cause a lower screw load, so they are desirable in spinning process.

After adjustment by Rabinowitsch correction, the flow curves showed a less steep running and a shift to higher shear rates. The lowest shear stress at the same shear rates after RC was demonstrated for masterbatch PLA1/bioPL. The remaining masterbatches had practically the same course (Figure 1b).

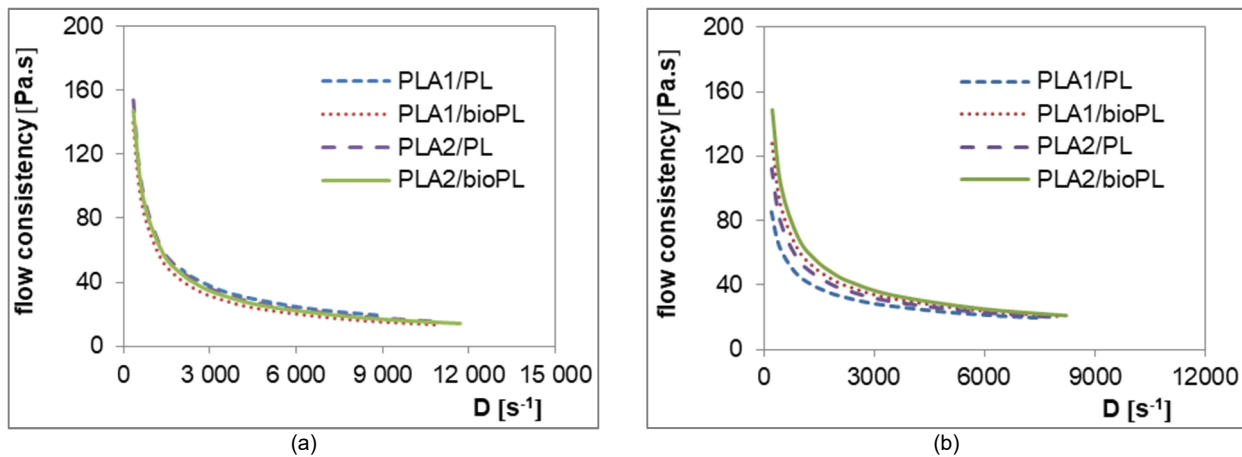
At 210°C the shear stress is lower compared to the shear stress at 190°C at the same shear rates. The shear stress at 210°C increases in order: masterbatch 1 (PLA1/PL) < 3 (PLA2/PL) < 2 (PLA1/bioPL) < 4 (PLA2/bioPL) in both calculated cases with and without Rabinowitsch correction (Figure 2). The results showed that the type of plasticizer more significantly affects the rheological properties at temperature of 210°C than at 190°C, where more the type of PLA polymer not additives influenced of the flow properties of the melt.



**Figure 1** Dependence of shear stress on the shear rate of PLA masterbatches with 15% additives (plasticizer PL, bioplasticizer bioPL) at temperature 190°C without (a) and with (b) Rabinowitsch correction



**Figure 2** Dependence of shear stress on the shear rate of PLA masterbatches with 15% additives (plasticizer PL, bioplasticizer bioPL) at temperature 210°C without (a) and with (b) Rabinowitsch correction



**Figure 3** The dependence of flow consistency (the real viscosity) on shear rate  $K=f(D)$  of PLA masterbatches with 15% additives (plasticizer PL, bioplasticizer bioPL) at temperature 190°C (a) and 210°C (b) after Rabinowitsch correction

In Newtonian fluids, the viscosity is only a material constant and does not depend on shear values, but only on the change in temperature. Because PLA masterbatches containing PL and bioPL are non-Newtonian pseudoplastic fluids with increasing shear rate, their viscosity decreases and changes with temperature (Figure 3).

From dependencies of flow consistency (the real viscosity) on shear rate  $K=f(D)$  of PLA masterbatches containing 15% additive at a melting point of 190°C in the whole range of shear rates the evaluated masterbatches have practically the same viscosities (Figure 3a). Slightly lower viscosity was observed for masterbatch 2 (PLA1/15%bioPL). At a melting point of 210°C, at low shear rates up to 3 000  $s^{-1}$  the viscosity of masterbatches decreases following  $4 > 2 > 3 > 1$ , which correspondent with shear rates of the evaluated masterbatches (Figure 2b).

The evaluation of the rheological properties of PLA masterbatches containing two types of additives PL

and bioPL, shows that the PLA1/PL masterbatch is from rheological point of view the most suitable for fibre preparation because it has the lowest flow consistency and thus good material fluidity as well as has the highest value of flow behavior index  $n$ . At the same time, melt of masterbatch 1 achieves at 210°C the lowest shear stress and viscosity from of all evaluated masterbatches at the same shear rates.

#### 4 CONCLUSION

The paper presents the results of masterbatches study, which consist of a mutual combination of two types of PLA polymers and two types of additives. The effect of the ingredients on the applicative and rheological properties of the masterbatches was investigated. The obtained experimental results were evaluated for the suitability of the masterbatches for the preparation of modified PLA fibres.

The results of the study showed that more the type of polymer as the type of additive used affects the applicative properties of the prepared masterbatches. Masterbatches prepared from PLA2 polymer have a lower *MFI* compared to masterbatches containing PLA1 polymer. Matrix degradation was detected in PLA2 masterbatches. A plasticizer PL showed a slight diluting effect of the in both types of PLA matrix used. The plasticizer bioPL does not affect the *MFI* of the PLA1 matrix. The filter index of all masterbatches is low; it is in the range of 35 - 185 MPa/kg, which means good dispersion of additives in the polymer matrix.

It follows from the above that the evaluated applicative properties of the studied PLA masterbatches will not negatively affect the technological stability of the fibre preparation process only degradation of the PLA2 matrix could have a negative effect on fibre formation.

The evaluation of the rheological properties of PLA masterbatches shows that the type of additive significantly affects the flow properties of masterbatches at 210°C, while at 190°C the flow properties of masterbatches are mainly influenced by the type of polylactic acid used.

The masterbatches containing plasticizer have higher values of the flow behavior index and lower flow consistency (lower viscosities) compared to masterbatches containing bioplasticizer, which indicates their better processability in fibre preparation. Due to better flow properties at temperature 210°C - lower shear stress and lower viscosity of investigated masterbatches, is a temperature regime 210°C more suitable for the processing of PLA masterbatches than temperature 190°C. Of all the masterbatches evaluated, the masterbatch prepared from PLA1 polymer and of plasticizer PL has the most suitable rheological characteristics. In terms of applicative and rheological properties, all masterbatches meet the technical conditions for the preparation of PLA fibres.

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