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Colour masterbatches and their use in polylactic acid fibres dyeing

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Abstract: This article is focused on the preparation of colour masterbatches from renewable sources based on polylactic acid, which were modified with inorganic pigments. Titanium dioxide, carbon black, and iron oxides were used as inorganic pigments. Due to the composition of the prepared colour PLA masterbatches, the influence of the inorganic pigment on the rheological and thermal properties was monitored. Rheological properties were determined using a capillary viscosimeter and a rotary rheoviscosimeter with a geometry plate/plate. The colour PLA masterbatches prepared in this way were subsequently used to dye polylactic acid fibres in the mass. The prepared fibres were drawn to the maximum drawn ratio λ_{max}. In case of fibres, the influence of composition and drawn ratio on thermal and mechanical properties was monitored.

Keywords: biodegradable polymers, inorganic pigment, mechanical properties, polylactic acid, rheological properties, thermal properties

Introduction

Polymeric materials obtained from petroleum sources are an integral part of life. They are mainly used in the food industry, agriculture, construction, medicine or in the automotive industry. The problem is that these materials are not biodegradable, they accumulate in landfills and pollute the environment. A good alternative are biodegradable polymers, which can decompose in nature and thus do not pollute the environment. Polylactic acid belongs to the best-known biodegradable polymers (Vroman and Tighzert, 2009).

Polylactic acid (PLA) is a linear aliphatic polyester derived from lactic acid which exists in two enantiomeric forms: D- and L-. Therefore, it is possible to produce polylactic acid from pure isomers of L- and D-lactic acid, when homopolymers of poly-L-lactic acid and poly-D-lactic acid are formed, or from a racemic mixture of L- and D-monomers, when a copolymer of poly- D, L-lactic acid is formed. PLA can be synthesised from lactic acid monomers by polycondensation, azeotropic dehydration condensation, ring-opening polymerisation reactions and enzymatic polymerisation. Ring-opening polymerisation reactions are the most widely used in industry due to the undemanding reaction conditions and the resulting polymers with high molecular weights. Polylactic acid can also be obtained by fragmentation from natural sources such as sugar beet, wheat, or corn (Casalini et al., 2019). Polylactic acid is characterised by high tenacity at break and high Young's modulus. However, it is a brittle material with low impact strength, low elongation at break, low thermal stability and poor barrier properties (Farah et al., 2016). PLA is a thermoplastic behaving as a solid substance at normal temperatures but changing at elevated temperatures into highly viscous liquids, which can be shaped and re-cooled to fix their shape. Thus, PLA can be processed by standard technologies such as extrusion, spinning, mixing, pressing, or injection molding, to produce fibres, foils, boards, cables, or 3D materials (Rasal et al., 2010).

Fibres made from polylactic acid belong to the most innovative textile materials and are increasingly in demand. PLA fibres are produced from renewable resources. Compared to fibres made from commercial polymers, PLA fibres are characterised by properties such as biodegradability, ease of processing, ease of composting and recycling, breathability, dyeability and stability against UV radiation (Yang et al., 2021). PLA fibres can be prepared by melt spinning, wet spinning, or electrospinning. One of the most used methods of PLA fibres preparation is melt spinning due to its simplicity and environmental friendliness (Gupta et al., 2007). Melt spinning is a process where solid polymer phase is formed from a polymer melt in the form of a fibre with primary structure. In the spinning process, the melt from the extruder is dosed and forced through holes of the spinning nozzle with a circular cross-section at a defined temperature and viscosity creating fine fibrils. The resulting fibrils solidify due to air cooling behind the nozzle. By pulling and winding these fibrils, endless fibres are prepared. However,

endless fibres do not have the required mechanical and physical properties necessary for further processing. Therefore, these fibres have to be drawn, which refers to axial deformation of a fibre in solid state under dynamic conditions. During drawing, macromolecules of the polymer chain are oriented in the direction of the applied deformation force. Orientation changes the physical and mechanical properties as well as the optical properties of the fibre. In addition to the change in properties, there is also a change in the geometry of the fibres, the length of the fibres increases and their diameter decreases. By drawing the fibres, tenacity at break and Young's modulus increase, while elongation at break decreases (Marcinčin, 1989; Rawal et al., 2014).

An important process of final treatment of polymer materials as well as fibres is their dyeing. Dyeing is a finishing process resulting in polymer materials of the required colour and thereby improved consumer properties. The colouring must be resistant to various influences of mechanical, chemical, or physical nature, to which the material is exposed during further technological processing or practical use, such as fastness to light, sweat, washing, water, abrasion, etc. PLA fibres can most often be dyed in two ways: by exhaust dyeing process from bath or in the mass. Exhaust dyeing process from bath consists of two phases, where the first phase consists of the fibre and the second of the dye bath. During the exhaust dyeing process from bath, diffusion, adsorption, and fixation of the dye from the dye bath onto the fibre occurs. However, from an ecological point of view, this method of dyeing is unacceptable because the discharge of waste substances from the dyeing process into rivers and streams causes pollution of water resources. In contrast to the exhaust dyeing process from bath, dyeing in the mass is a better option because the dye is incorporated into the polymer melt during fibre production, not polluting water sources and with better dyeability of the fibre. When dyeing in the mass, dyes are used in the form of powders, pastes or in granulated form, so-called colour masterbatches (Balakrishnan, 2020; Grishanov, 2011; Prchal, 1993; Trotman, 1970), which is the most widespread method of dyeing fibres in the mass. Advantages of this dyeing method include dust-free environment, good dosage, trouble-free increase in pigment content, and optimal use of colour strength. Colour masterbatches are processed to impart colour, texture, and various other properties to the polymer materials to which they are applied. Colour masterbatches are composed of three basic components: the carrier, the dispersing agent, and the pigment. In addition to these components, other additives can be included, such as various antistatic agents, antibacterial agents, nucleating agents, stabilizers, wetting agents, and others. The carrier is a polymer compatible with the dispersant and the pigment (Parra-Campos et al., 2020; Benetti et al., 2014). Dispersing agents are substances necessary for the dispersion and homogenisation of pigments in the preparation of colour concentrates. Without these substances, pigments in the polymer mass form unwetted agglomerates, which render the workability of colour concentrates unsatisfactory (Hricová et al., 2004). In general, pigments are fine coloured powders, the resulting colour of which is determined by the spectrum of reflected wavelengths of light. Pigments are insoluble in the polymer matrix, and are dispersed as fine particles (Koenig et al., 2020; Markarian, 2009). Pigments are inorganic and organic; inorganic pigments have high thermal stability and good light stability compared to organic pigments (Tolinski, 2009). Since coloured fibres were prepared from polylactic acid, which is a biodegradable polymer, it is necessary to use also biodegradable colour masterbatches (Chen, 2018). Therefore, in the production of colour masterbatches, polylactic acid was used as a carrier in combination with inorganic pigments, specifically titanium dioxide, carbon black, and iron oxides, which are biodegradable and can be obtained from renewable sources. In the preparation of colour masterbatches, mixing and homogenisation play an important role in achieving the best possible dispersion. Mixing is represented by two basic processes – distributive and dispersive mixing. During distributive mixing, homogeneous distribution of the pigment is achieved inside the polymer matrix. The process of distributive mixing depends on the magnitude of the shear deformations and the intensity of mass transport in the mixing device. During dispersion mixing, agglomerates break down into primary particles. Considering dispersive mixing, the size of the shear deformation is not important, the determining factor is the size of the shear stress, which ensures the disintegration of agglomerates into primary particles. In order for the agglomerates to break down into primary particles, cohesive forces between the agglomerate particles must weaken (Balakrishnan et al., 2022; Benetti et al., 2014; Niaounakis, 2015).

Rheological properties of polymers and colour PLA masterbatches are important from the point of view of their processing. Most polymer processing technologies are based on their processing in the melt, when the polymer flows (Alexy, 2016). Further processing of the prepared PLA masterbatches used for PLA fibres dyeing in the mass, requires the knowledge of rheological and thermal proper-

ties of the prepared colour PLA masterbatches. Properties of the prepared PLA masterbatches subsequently affect the processability of PLA during fibre preparation. PLA fibres are an oriented system unlike colour PLA masterbatches, which are a non-oriented system. Therefore, with PLA fibres, in addition to the influence of the composition, also the influence of the drawn ratio on thermal and mechanical properties was monitored.

Materials and Methods

Materials used

Polymer

Polylactic acid INGEO I6100D (**PLA6100**) is a thermoplastic fibre-grade resin (in pellet form) derived primarily from annually renewable resources, *MFI* = 24g/10 min at 210 °C, glass temperature T_g = 55—60 °C, melting temperature T_m = 165—180 °C (produced by NatureWorks LLC).

Inorganic pigments

1. titanium dioxide Pretiox AV01SF (**Ti**) is ultrafine milled anatase TiO_2 without surface treatment, primary particle size (TEM) of 21 nm, T_m = 1850 °C (produced by Precheza a.s.);
2. carbon black Printex Alpha (**PXA**) is a fine black powder with high specific area, average primary particle size of 20 nm, T_m > 3000 °C (produced by Orion Engineered Carbons GmbH);
3. iron oxide Fepren TP 303 (**Fe**) is a fine dry-milled pigment with very high tinting-strength, particle size <50 nm (BET), T_m = 1565 °C (produced by Precheza a.s.).

Silicone oil V350 was used as dispersing agent (produced by Azelis Slovakia, s.r.o.).

Colour masterbatches preparation

A laboratory line with twin-screw extruder WP ZDSK (screw diameter of 28 mm), in vacuum zone and in the temperature range of 180—210 °C, was used for the preparation of PLA colour masterbatches. Final concentration of inorganic pigments in the prepared masterbatches was 1 and 3 wt %.

Fibres preparation

Before spinning, pure PLA granulate and pigmented PLA masterbatches were dried in a laboratory oven for 3 hours at 60 °C. Pure PLA fibres and pigmented PLA fibres with the final concentration of pigments of 0.1 and 0.5 wt % were prepared using a laboratory spinning plant at 190 °C with the take-up speed of 150 $m \cdot min^{-1}$.

After spinning, the prepared PLA fibres and pigmented PLA fibres were drawn using a laboratory drawing machine at the maximal drawn ratio λ_{max} at drawing temperatures T_{dr} = 95 °C and T_{dr} = 105 °C. Composition of fibres and obtained drawn ratios are presented in Table 1.

Methods used

Rheological properties

Rotary rheoviscosimeter Physica MCR 101 (Anton Paar) was used to measure rheological behaviour of pure PLA and pigmented PLA masterbatches. Parallel plate geometry was used applying the diameter of 25 mm and the gap set to 1 mm. All rheological measurements were performed in air atmosphere at 190 °C and at 1 % strain from 0.1 to 100 $rad \cdot s^{-1}$.

Moreover, rheological properties of PLA and pigmented PLA masterbatches were measured using a capillary viscosimeter GÖTTFERT RG20 at 190 °C. The conditions of measurement: capillary with the circular diameter with L/D = 30/1 and a piston with the diameter of 15 mm was used in the range of shear speeds from 90 to 4500 s^{-1} with preheating for 5 minutes.

Thermal properties

Thermal properties were measured by DSC 1/750 with ceramic sensor FRS5 using software SW STARe by Metler Toledo. Conditions used in the measurement were: 1st heating: 20—190 °C, isothermally held for 3 minutes, cooling: 190—20 °C,

Tab. 1. Composition of PLA fibres with 0.1 and 0.5 wt % pigments with drawing temperatures T_{dr}, maximal drawn ratios λ_{max} and fineness of fibres T_t.

Composition of fibres	T_{dr} [°C]	λ_{max}	T_t [tex]
PLA6100	105	3.5	23.2
PLA6100+0.1 %Ti		3.6	20.1
PLA6100+0.1 %PXA	105	3.3	18.9
PLA6100+0.1 %Fe		3.4	18.1
PLA6100+0.5 %Ti		2.5	41.5
PLA6100+0.5 %PXA	95	2.5	49.8
PLA6100+0.5 %Fe		2.5	42.5

isothermally held for 3 minutes, 2nd heating: 20–190 °C. The rate of heating or cooling was 10 °C/min. The measurements were done in inert nitrogen atmosphere. From the measured thermograms, glass temperature (T_g), cold crystallisation temperature (T_{cc}), melting temperature (T_m), enthalpy of relaxation (ΔH_{er}), enthalpy of melting (ΔH_m) and enthalpy of cold crystallisation (ΔH_{cc}) obtained during the 1st heating and the crystallisation temperature (T_c) and enthalpy of crystallisation (ΔH_c) obtained during cooling were evaluated. During the 2nd heating, glass temperature (T_g), cold crystallisation temperature (T_{cc}), melting temperature (T_m), enthalpy of relaxation (ΔH_{er}), enthalpy of melting (ΔH_m), and enthalpy of cold crystallisation (ΔH_{cc}) were evaluated.

Mechanical properties

Mechanical properties (tenacity and elongation at break as well as Young's modulus) of PLA and pigmented PLA fibres were evaluated by Instron 3343 equipment and the mechanical characteristics were determined from 15 measurements according to ISO 2062:1993. The initial length of fibres was 125 mm and the time of deformation was about 20 sec.

Results and discussion

Rheological properties of colour masterbatches

Rheological properties of polymer materials and colour masterbatches are important for their processing. The influence of type (Ti, PXA, Fe) and concentration (1 and 3 wt %) of inorganic pigments on the rheological properties of colour masterbatches was monitored. Rheological properties were determined using a capillary viscosimeter and a rotary rheoviscosimeter with a geometry plate/plate. Dependences of viscosity on shear rate were constructed from the measured values and are

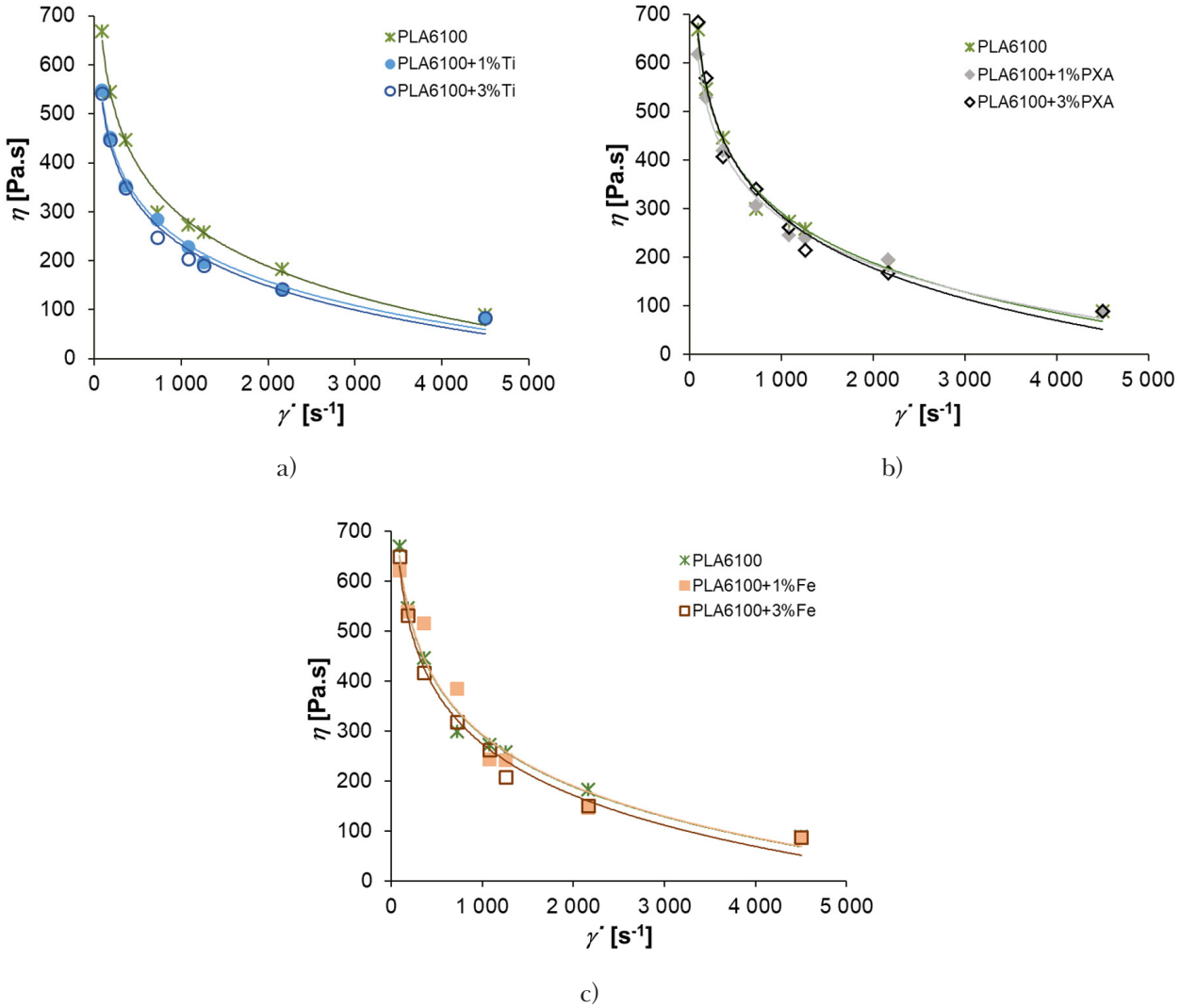


Fig. 1. Dependence of viscosity η on shear rate $\gamma^{\cdot}$ obtained on the capillary viscosimeter for colour PLA masterbatches with 1 and 3 wt % of inorganic pigments: Ti (a), PXA (b), Fe (c).

shown in Figures 1 and 2 for the capillary viscosimeter (Figure 1) and for the rotary rheoviscosimeter with a geometry plate/plate (Figure 2) for colour masterbatches modified with 1 and 3 wt % of inorganic pigments, which show viscosity decrease with the increasing shear rate. Viscosity is defined as the ratio of shear stress to shear rate, implying that the higher the shear rate applied to the material, the faster the material flow and thus lower viscosity. As it can be seen, viscosity is not constant as in the case of Newtonian substances but varies with the shear rate. This is typical for pseudoplastic materials with non-Newtonian behaviour. Based on this, the prepared colour masterbatches modified with inorganic pigments can be considered as pseudoplastic substances.

Figure 1 shows the dependences of viscosity on the shear rate of the prepared colour PLA masterbatches modified with 1 and 3 wt % of inorganic pigments (Ti, PXA, Fe) measured on the capillary viscosimeter. Colour PLA masterbatches are pseudoplastic substances with non-Newtonian behaviour and therefore, the Rabinowitsch correction was used when measuring rheological properties, which takes into account the Newtonian nature of the flow on the capillary wall. In Figure 1a, a decrease in viscosity due to the addition of inorganic pigment Ti was observed comparing pure PLA6100 with PLA6100 masterbatches with 1 and 3 wt % of Ti. A comparison of PLA6100 masterbatch with 1 wt % of inorganic pigment Ti and with 3 wt % of Ti shows that the higher the content of inorganic pigments (3 wt %), the greater the drop in viscosity. In Figures 1b and 1c, small changes in the dependences of viscosity on shear rate when comparing pure PLA6100 with PLA6100 masterbatches with 1 and 3 wt % of inorganic pigments PXA and Fe can be seen.

Figure 2 shows the dependences of viscosity on the shear rate of the prepared colour PLA master-

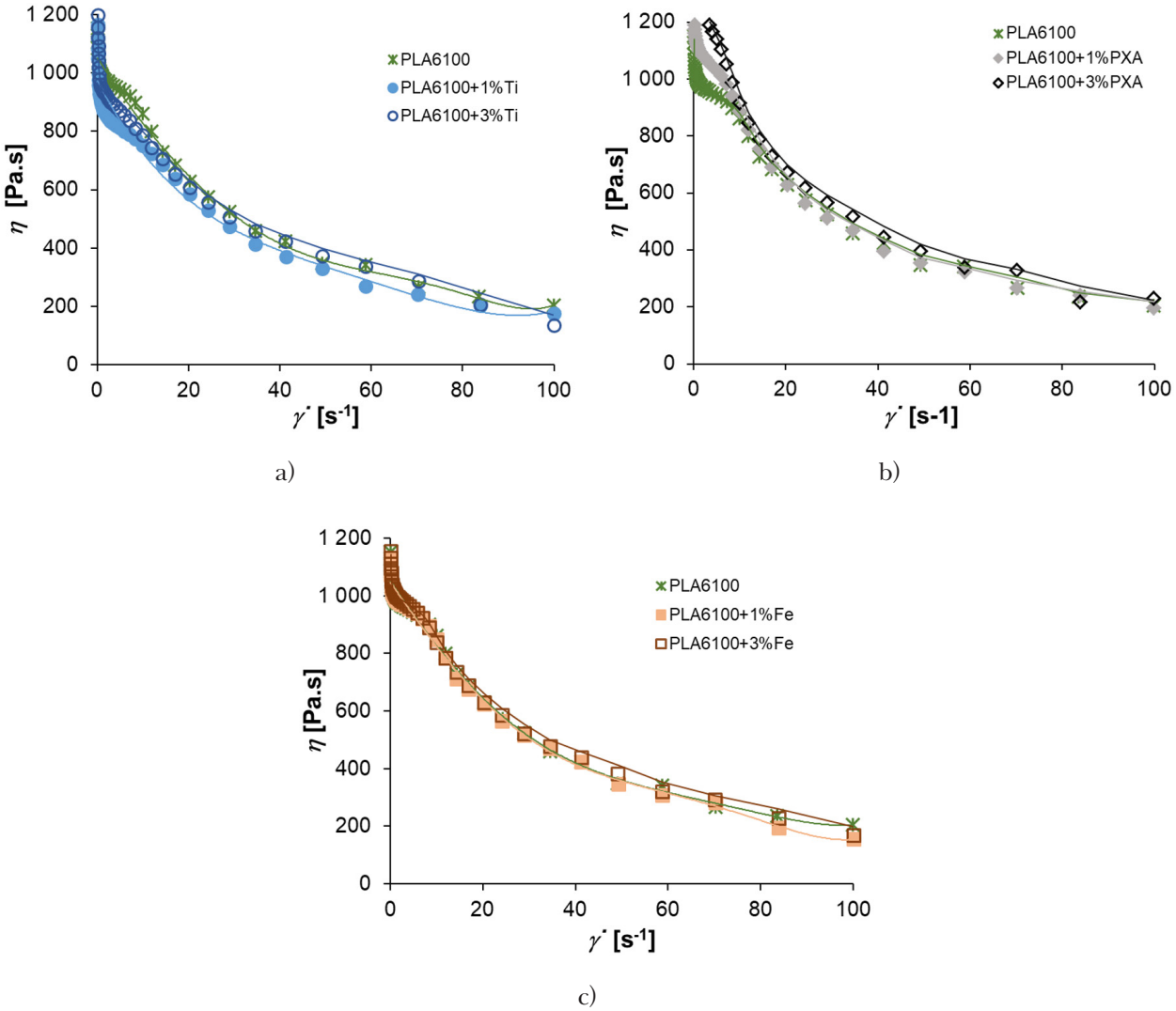


Fig. 2. Dependence of viscosity η on shear rate $\dot{\gamma}$ obtained on the plate/plate rotary rheoviscosimeter for colour PLA masterbatches with 1 and 3 wt % of inorganic pigments: Ti (a), PXA (b), Fe (c).

batches with 1 and 3 wt % of inorganic pigments (Ti, PXA, Fe) measured on the rotary rheoviscosimeter with a geometry plate/plate. A comparison of PLA6100 masterbatches with 1 wt % of Ti (Figure 2a), PXA (Figure 2b), and Fe (Figure 2c) with those with 3 wt % of Ti (Figure 2a), PXA (Figure 2b) and Fe (Figure 2c), revealed an increase in the viscosity due to the addition of a higher content of inorganic pigments (3 wt %). In Figure 2a, a decrease in viscosity, which is more visible at low shear rates, is observed comparing pure PLA6100 with PLA6100 masterbatches with 1 and 3 wt % of Ti. Figure 2b shows an increase in viscosity due to the addition of PXA comparing pure PLA6100 with PLA6100 masterbatch with 3 wt % of PXA. The observed increase in viscosity caused by adding PXA compared to other pigments (Ti, Fe) can be evaluated considering different chemical structure, chemical properties, size of pigment particles, shape of pigment particles, and intermolecular interactions between pigment particles. It can be assumed that, as the content of inorganic PXA pigment increases, the dispersibility of PXA particles in the polymer matrix deteriorates and they remain aggregated which results in an increase in viscosity. By adding 1 or 3 wt % of Fe to pure PLA6100, minimal differences in the dependences of viscosity on the shear rate were observed.

Thermal properties of colour PLA masterbatches and PLA fibres

Thermal properties of prepared colour PLA masterbatches and PLA fibres were determined by DSC analysis by monitoring endothermic and exothermic processes. From the measured thermograms, basic thermal parameters such as glass temperature (T_g), cold crystallisation temperature (T_{cc}), melting temperature (T_m), crystallisation temperature (T_c), enthalpy of relaxation (ΔH_{er}), enthalpy of melting (ΔH_m), enthalpy of crystallisation (ΔH_c), and enthalpy of cold crystallisation (ΔH_{cc}) of the prepared colour PLA masterbatches and PLA fibres obtained during the 1st (Tables 2 and 4) and 2nd (Tables 3 and 5) heating were evaluated. During the 1st heating, thermal history of colour PLA masterbatches and PLA fibres, related to their preparation and storage, was cancelled. The following cooling allowed the formation of a new structure. The second heating is important for the characterisation of the examined colour PLA masterbatches and PLA fibres. During the 2nd heating, thermal properties of the colour PLA masterbatches and PLA fibres were monitored. To determine the properties of colour PLA masterbatches and PLA fibres, results from the 1st heating were compared. To determine the influence of the addition of 1 and 3 wt % pigment content in PLA masterbatches and 0.1 and 0.5 wt % pigment content in PLA fibres, results from the 2nd heating were compared.

When evaluating thermal properties of colour PLA masterbatches (Tables 2 and 3), PLA6100 masterbatches with 1 or 3 wt % of inorganic pigments showed lower glass temperature T_g than pure PLA during the 1st heating. The decrease in T_g of PLA colour masterbatches is due to the addition of inorganic pigments that act as nucleating agents, promote crystallisation, and increase the crystallinity thus decreasing T_g. The increased content of inorganic pigments (3 wt %) does not affect the glass temperature. During the 1st heating, PLA masterbatches showed higher value of the enthalpy of relaxation than pure PLA, which can be explained by weak interactions formed between the polymer carrier (PLA) and inorganic pigments during the preparation of colour masterbatches. Increased enthalpy of relaxation and decreases T_g. During the 1st heating, cold crystallisation was measured for all PLA masterbatches with 1 and 3 wt % of inorganic

Tab. 2. Glass temperature (T_g), cold crystallisation temperature (T_{cc}), melting temperature (T_m), enthalpy of relaxation (ΔH_{er}), enthalpy of cold crystallisation (ΔH_{cc}), and enthalpy of melting (ΔH_m) of prepared colour masterbatches obtained during the 1st heating, and crystallisation temperature (T_c) and enthalpy of crystallisation (ΔH_c) of prepared colour masterbatches obtained during cooling

Composition of masterbatches	1st heating								Cooling	
	T_g [°C]	ΔH_{er} [J/g]	T_{cc1} [°C]	ΔH_{cc1} [J/g]	T_{cc2} [°C]	ΔH_{cc2} [J/g]	T_m [°C]	ΔH_m [J/g]	T_c [°C]	ΔH_c [J/g]
PLA6100	68.4	0.6	–	–	163.1	1.7	176.7	37.6	103.8	0.5
PLA6100+1 %Ti	63.5	4.7	94.8	24.4	161.2	3.5	176.5	17.4	103.4	20.1
PLA6100+3 %Ti	64.4	4.9	94.8	22.6	161.1	3.1	176.4	19.0	93.6	9.6
PLA6100+1 %PXA	65.8	6.1	98.2	24.1	161.6	3.2	176.8	18.6	88.4	3.3
PLA6100+3 %PXA	65.8	5.7	101.9	26.5	162.5	2.8	177.4	14.4	100.4	1.3
PLA6100+1 %Fe	64.1	5.2	95.4	24.6	160.9	3.5	176.9	16.4	91.1	8.5
PLA6100+3 %Fe	63.0	3.5	95.9	23.0	161.2	3.2	177.3	17.0	92.4	5.1

pigments. The presence of pigments contributes significantly to cold crystallisation because no cold crystallisation was observed in pure PLA6100. Endothermic peak with a maximum at 176.7 °C, corresponding to the melting temperature, was detected during the 1st heating (Table 2). Comparing the melting temperature obtained during the 1st heating of pure PLA6100 with those of PLA6100 masterbatches with 1 and 3 wt % of inorganic pigments (Ti, PXA, Fe), minimal differences in melting temperatures were detected. During the 1st heating, a decrease in the enthalpy of melting of PLA masterbatches due to an addition of inorganic pigments was observed. Exothermic peak with a maximum at 103.8 °C, corresponding to the crystallisation temperature, was detected during the cooling of pure PLA (Table 2). Crystallisation of colour PLA masterbatch occurred at significantly lower temperatures. A comparison of pure PLA6100 with PLA6100 masterbatches with 1 and 3 wt % of inorganic pigments showed an increase in the enthalpy of crystallisation during cooling caused by the addition of inorganic pigments.

During 2nd heating, glass temperature T_g of pure PLA and PLA masterbatches was maintained and an increase in the enthalpy of melting of PLA masterbatches due to the addition of inorganic pigments was observed. This difference can be explained by a change in the formation of different crystalline modifications of PLA. During the 2nd heating, pure PLA6100 showed cold crystallisation with a maximum exothermic peak at 128.1 °C (Table 3), while for colour PLA masterbatches, cold crystallisation occurs at lower temperatures (94—104 °C) and shows another peak of cold crystallisation at 159—161 °C, where pure PLA does not crystallize.

Comparing melting temperature T_m of the 1st heating with that of the 2nd heating, a slight decrease in the melting temperature during the 2nd heating for both pure PLA6100 and for PLA6100 masterbatches can be seen.

The addition of pigments showed no effect on T_g and the differences in T_g are minimal (Tables 4 and 5). Crystallisation temperature of pure PLA fibres and of PLA fibres with 0.1 and 0.5 wt % of inorganic pigments revealed minimal differences.

Tab. 3. Glass temperature (T_g), cold crystallisation temperature (T_{cc}), melting temperature (T_m), enthalpy of relaxation (ΔH_{er}), enthalpy of cold crystallisation (ΔH_{cc}), and enthalpy of melting (ΔH_m) of prepared colour masterbatches obtained during the 2nd heating.

Composition of masterbatches	2nd heating							
	T_g [°C]	ΔH_{er} [J/g]	T_{cc1} [°C]	ΔH_{cc1} [J/g]	T_{cc2} [°C]	ΔH_{cc2} [J/g]	T_m [°C]	ΔH_m [J/g]
PLA6100	62.1	1.5	128.1	15.0			173.9	6.5
PLA6100+1 %Ti	62.1	0.5	94.0	7.9	159.7	2.1	174.5	34.7
PLA6100+3 %Ti	61.9	0.8	94.2	11.8	159.3	3.4	173.8	29.5
PLA6100+1 %PXA	62.1	1.3	94.7	21.5	158.9	3.7	174.1	21.7
PLA6100+3 %PXA	62.2	1.4	103.5	26.3	161.3	3.3	174.3	14.7
PLA6100+1 %Fe	62.0	0.9	93.9	16.8	159.2	3.2	174.2	27.7
PLA6100+3 %Fe	61.9	1.3	94.5	18.5	159.4	3.7	174.0	22.3

Tab. 4. Glass temperature (T_g), crystallisation temperature (T_c), enthalpy of crystallisation (ΔH_c) melting temperature (T_m), and enthalpy of melting (ΔH_m) of prepared colour masterbatches obtained during the 1st heating, and crystallisation temperature (T_c) and enthalpy of crystallisation (ΔH_c) of prepared colour masterbatches obtained during cooling.

Composition of fibres	1st heating					Cooling	
	T_g [°C]	T_c [°C]	ΔH_c [J/g]	T_m [°C]	ΔH_m [J/g]	T_c [°C]	ΔH_c [J/g]
PLA6100	56.3	74.7	2.3	174.4	41.9	98.9	27.8
PLA6100+0.1 %Ti	55.8	74.6	2.8	173.7	47.5	98.5	30.5
PLA6100+0.5 %Ti	58.9	75.7	16.6	172.4	32.5	99.6	33.4
PLA6100+0.1 %PXA	57.3	77.1	2.4	174.5	46.7	96.6	32.5
PLA6100+0.5 %PXA	59.1	76.2	15.8	173.4	32.0	95.4	31.4
PLA6100+0.1 %Fe	56.8	74.1	2.2	173.4	48.9	98.2	31.1
PLA6100+0.5 %Fe	58.9	76.0	10.6	172.2	37.2	95.7	30.3

During the 1st heating, PLA fibres with 0.1 wt % pigment content showed the enthalpy of crystallisation decrease with an increase in the drawn ratio due to the change in the crystalline modification and orientation of PLA. Cold crystallisation was measured for all PLA fibres with 0.1 and 0.5 wt % of all three inorganic pigments. Endothermic peak with maximum at 174.4 °C, corresponding to the melting temperature, was detected during the 1st heating. The addition of a higher pigment content (0.5 wt %) resulted in a decrease in the enthalpy of melting. PLA fibres with the 0.1 wt % pigment content were drawn at a higher temperature with higher values of maximum drawn ratios. Considering an oriented system, the enthalpy of melting increases with the increasing temperature, which is probably due to higher orientation leading to higher crystallisation ability. In regard to pigment addition, 0.1 wt % of pigment behaves as a nucleating agent that promotes the crystallisation process and increases the crystallinity.

Exothermic peak with a maximum at 98.9 °C, corresponding to the crystallisation temperature, was detected during the cooling (Table 4). Comparison of pure PLA fibres with pigmented PLA fibres, an increase in the enthalpy of crystallisation during cooling due to inorganic pigments addition was observed.

During the 2nd heating (Table 5), changes in the glass temperature of pure PLA fibres and those with 0.1 and 0.5 wt % pigment content were not observed. Since PLA is a semi-crystalline polymer, crystallisation during the 2nd heating results in a decrease in the content of the amorphous phase and an increase in the content of the crystalline phase, thereby eliminating the manifestation of T_g which is related to the amorphous phase.

Comparing the melting temperature obtained during the 1st and 2nd heating of pure PLA fibres and of PLA fibres with 0.1 and 0.5 wt % of inorganic pigments, minimal differences in the melting temperature were observed. The enthalpy of melting obtained during the 1st and 2nd heating of pure PLA fibres and of PLA fibres with 0.1 and 0.5 wt % of inorganic pigments decreased during the 2nd heating.

Mechanical properties of PLA fibres

The effect of the addition of 0.1 and 0.5 wt % of inorganic pigments (Ti, PXA, Fe) on mechanical properties such as tenacity at break σ, elongation at break ε, and Young's modulus E for PLA fibres drawn to maximum drawn ratio λ_{max} was monitored and the dependencies of tenacity at break, elongation at break, and Young's modulus on fibres composition were constructed(Figures 3a–c). Fineness of individual PLA fibres and pigmented PLA fibres was measured and the dependence of fineness of fibres T_t on their composition was constructed (Figure 3d).

The maximum drawn ratio of PLA fibres was significantly affected by the concentration of pigments; 0.1 wt % of pigments had minimal or positive effect on the values of λ_{max} at the drawing temperature of 105 °C. The higher pigment content (0.5 wt %) caused worsening of the drawing process and PLA fibres with 0.5 wt % of pigment content could not be drawn at the drawing temperature of 105 °C; instead, drawing temperature of 95 °C was used. At the drawing temperature of 95 °C, the maximum drawn ratio for all pigmented PLA fibres dropped to λ_{max} = 2.5 (see Table 1).

The tenacity at break of fibres is defined as the force required to break the fibre relative to the fineness of the fibres. From the dependencies in Figure 3a, an increase in the tenacity at break of fibres due to the addition of 0.1 wt % of pigment content to pure PLA fibres can be seen. This is probably caused by the pigment acting as a nucleating agent

Tab. 5. Cold crystallisation temperature (T_{cc}), melting temperature (T_m), enthalpy of cold crystallisation (ΔH_{cc}) and enthalpy of melting (ΔH_m) of prepared colour masterbatches obtained during the 2nd heating.

Composition of fibres	2nd heating					
	T_{cc1} [°C]	ΔH_{cc1} [J/g]	T_{cc2} [°C]	ΔH_{cc2} [J/g]	T_m [°C]	ΔH_m [J/g]
PLA6100	119.5	1.6	157.9	1.5	173.7	34.7
PLA6100+0.1 %Ti	106.9	3.9	156.9	2.1	172.9	38.5
PLA6100+0.5 %Ti	111.2	5.1	157.3	0.1	173.1	36.5
PLA6100+0.1 %PXA	118.9	5.6	158.3	1.7	173.1	35.7
PLA6100+0.5 %PXA	105.3	5.4	157.3	2.3	172.6	34.7
PLA6100+0.1 %Fe	116.8	2.3	156.8	2.6	172.8	40.9
PLA6100+0.5 %Fe	118.3	2.5	156.9	1.8	172.8	38.2

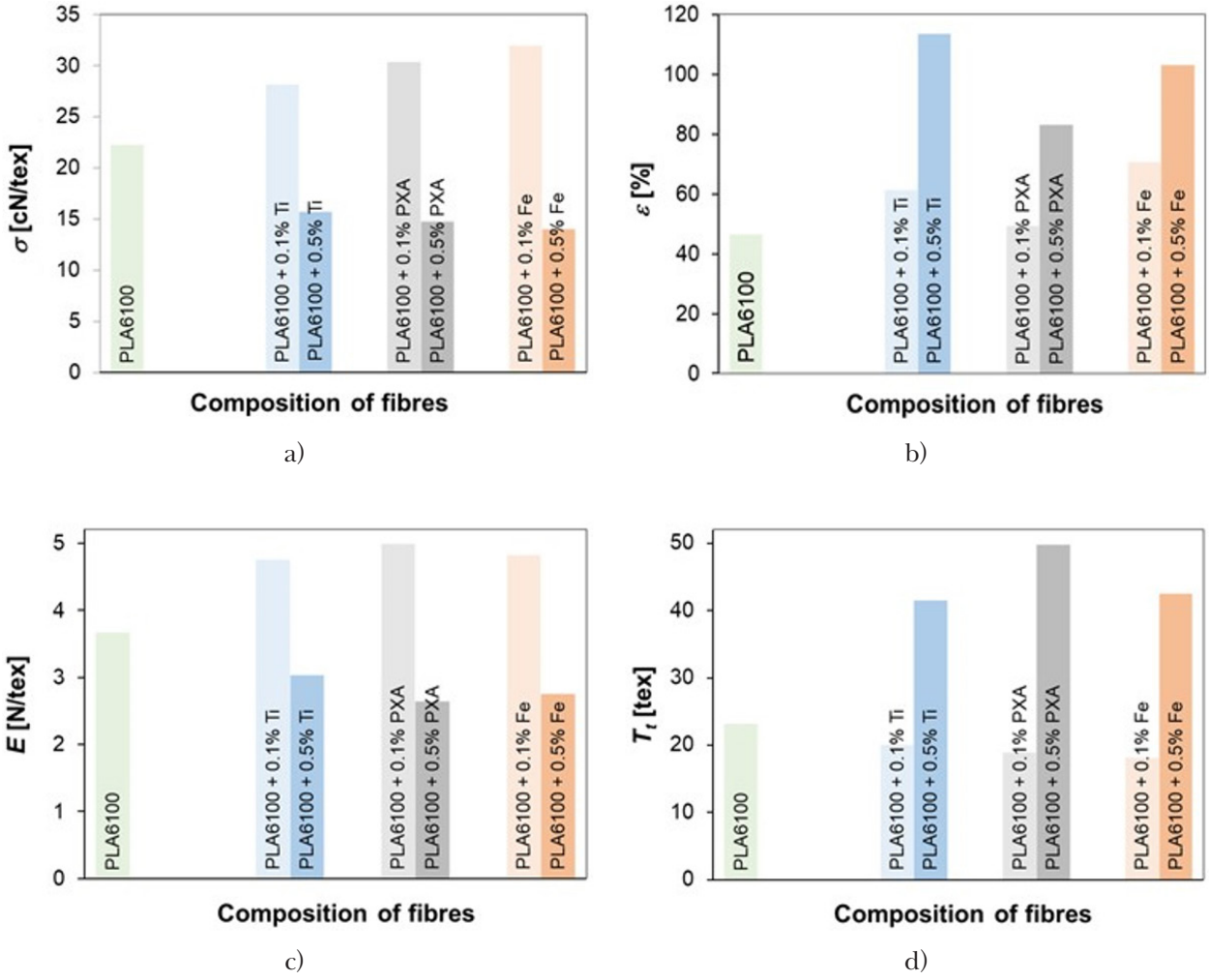


Figure 3. Dependence of tenacity at break σ (a), elongation at break ε (b), Young's modulus E (c), and fineness of fibres T_t (d) on PLA fibres composition

at 0.1 wt %, thus increasing the crystallinity and improving mechanical properties of the fibres. At the higher pigment content of 0.5 wt %, a decrease in the tenacity at break of PLA fibres can be observed. Higher pigment content can lead to higher agglomeration of pigment particles, worsening thus the mechanical properties of the fibres. From the point of view of drawing temperature, an increase in the tenacity at break of fibres was observed in PLA fibres with 0.1 wt % pigment content drawn at 105 °C compared to those with 0.5 wt % pigment content drawn at 95 °C due to the increased drawing temperature. At higher drawing temperatures, fibres with higher orientation were prepared. Higher orientation of the chains causes tighter arrangement of macromolecules, thereby increasing the number and strength of intermolecular interactions, which is reflected in higher tenacity at break of fibres. A comparison of the dependence of tenacity at break on fibres composition (Figure 3a) with that of the dependence of elongation at break (Figure 3b), elongation at break of fibres has been confirmed to decrease with the increasing tenacity at break of fibres.

The elongation at break of fibres is given by the greatest elongation that the material achieves when it breaks. From the dependence of elongation at break on fibres composition (Figure 3b), an increase in the elongation at break of fibres with 0.1 and 0.5 wt % pigment content was observed compared to pure PLA fibres. The highest effect of the addition of pigments was observed in PLA fibres with 0.5 wt % pigment content. The higher the pigment content, the higher the elongation at break of fibres.

Young's modulus was another monitored quantity, it is a measure of resistance to deformation and depends on crystallinity and orientation. From the dependence of Young's modulus on fibres composition (Figure 3c), it can be seen that all PLA fibres containing 0.1 wt % of pigments have higher modulus than pure PLA fibres, while a decrease

in Young's modulus in PLA fibres with 0.5 wt % pigment content was observed. All PLA fibres containing 0.5 wt % of pigments were drawn at the maximum drawn ratio λ_{max} = 2.5 at 95 °C. It follows that oriented systems with lower drawn ratio have lower Young's modulus.
From the dependence of fineness on fibres composition (Figure 3d), PLA fibres containing 0.1 wt % of pigments have shown lower fineness than pure PLA fibres, while an increase in fineness of PLA fibres with 0.5 wt % pigment content was detected.

Conclusion

This work was focused on the preparation of colour PLA masterbatches and PLA fibres. The influence of inorganic pigments on the rheological and thermal properties of the prepared colour PLA masterbatches and that of colour PLA masterbatches composition and PLA fibres drawn ratio on thermal and mechanical properties of PLA fibres were determined. Properties of the prepared PLA masterbatches subsequently affect the processability of PLA during fibre preparation. Based on the obtained data, the results can be formulated into the following conclusions:

1. Rheological properties of colour PLA masterbatches were determined using a capillary viscosimeter and a rotary rheoviscosimeter with geometry plate/plate. By adding 1 or 3 wt % of inorganic pigments PXA and Fe to pure PLA6100, small changes in the dependences of viscosity on shear rate were obtained on the capillary viscosimeter. A more significant drop in viscosity was detected after the addition of Ti to pure PLA compared to other pigments (PXA, Fe). An increase in the viscosity (dependences of viscosity on shear rate obtained on the rotary rheoviscosimeter with a geometry plate/plate) due to the addition of a higher pigment content (3 wt %) was observed compared to colour PLA masterbatches with 1 wt % pigment content. The largest increase in viscosity was observed when 3 wt % of PXA were added to pure PLA.
2. Thermal properties of prepared colour PLA masterbatches and PLA fibres were determined by DSC analysis. By adding 1 or 3 wt % pigment content to pure PLA6100, a drop in T_g of colour PLA masterbatches during the 1st heating was observed. The increased content of inorganic pigments (3 wt %) does not affect the glass temperature. During the 1st heating, cold crystallisation was measured for colour PLA masterbatches with all three pigments. During the 2nd heating, pure PLA6100 showed cold crystallisation with a maximum exothermic peak at 128.1 °C. And with colour PLA masterbatches, cold crystallisation occurs at lower temperatures (94—104 °C) and shows another peak of cold crystallisation at temperatures of 159—161 °C, where pure PLA does not crystallize. Considering the thermal properties of PLA fibres, the addition of pigment has no effect on T_g and the differences of T_g are minimal. During the 1st heating, cold crystallisation was measured for all pigmented PLA fibres with 0.1 and 0.5 wt % pigment content. An increase in the enthalpy of crystallisation during cooling due to the addition of inorganic pigments occurred. During the 1st heating, the addition of a lower pigment content (0.1 wt %) resulted in an increase in the enthalpy of melting, which increases with the increasing drawing temperature. A comparison of the enthalpy of melting obtained during the 1st and the 2nd heating of pure PLA fibres and of PLA fibres with 0.1 and 0.5 wt % of inorganic pigments, revealed a decrease in the enthalpies of melting during the 2nd heating.
3. A comparison of PLA fibres with 0.1 wt % pigment content drawn at 105 °C with PLA fibres with 0.5 wt % pigment content drawn at 95 °C showed an increase in the tenacity at break of fibres due to increased drawing temperature. A decrease in the tenacity at break of PLA fibres with higher (0.5 wt %) pigment content was observed. Higher pigment content can lead to a higher agglomeration of pigment particles, thus worsening the mechanical properties of the fibres. The highest effect on elongation at break was observed in PLA fibres with 0.5 wt % pigment content. The higher the pigment content, the higher the elongation at break of fibres. By comparing PLA fibres with 0.1 wt % pigment content and those with 0.5 wt % pigment content, a decrease in Young's modulus was detected for PLA fibres with 0.5 wt % pigment content. All PLA fibres containing 0.5 wt % of pigments were drawn at the maximum drawn ratio λ_{max} = 2.5 at 95 °C. It follows that oriented systems with lower drawn ratio have lower Young's modulus. By adding 0.5 wt % of pigment to pure PLA fibres, an increase in PLA fibres fineness can be seen.

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