INFLUENCE OF PLASTICIZER AND BIOPLASTICIZER ON THE STRUCTURE AND MECHANICAL PROPERTIES OF THE PLA FIBRES

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Abstract: *Nowadays, when great accent is placed on the ecology and thus also on biodegradable materials, the polylactic acid (PLA) proves to be one of the prospective materials for packaging and fibre industries. Brittleness of the PLA has a negative effect on the physical-mechanical properties of the fibres, which prevents its mass utilization in this field. Therefore, new solutions to reduce the brittleness of PLA fibres are constantly being sought. In this work, the influence of plasticizer and bioplasticizer contents on the structure and mechanical properties of PLA fibres was studied and compared. The advantage of the bioplasticizer is to ensure complete degradation of the PLA fibres under special conditions. From the structural properties, the birefringence and crystallinity were investigated and from the mechanical properties, the tensile strength, elongation at break and Young's modulus were studied. The modified PLA fibres were prepared by a discontinuous process of spinning and drawing.*

Keywords: *modified PLA fibres, structure, mechanical properties, plasticizer, bioplasticizer.*

1 INTRODUCTION

The high increase in global polymer production in the 20th century has led to the depletion of oil reserves, increased greenhouse gas emissions and the accumulation of polymer waste which also include textile materials made from synthetic polymers such as polypropylene, polyamide and polyester, which have excellent resistance to external influences. Due to the current crisis in the accumulation of solid polymer waste, the resistance of polymers is becoming a disadvantage and therefore the 21st century is focused on materials that will decompose in the natural environment, in soil or compost [1-4]. One of them is also fully biodegradable polymers polylactic acid (PLA) [5] which attract of various markets e.g. textile, packaging and automotive industries, as an eco-alternative to traditional petroleum-based commodity polymers [6-8].

Plasticizers or dispersants are additives that increase the plasticity or decrease the viscosity of a material. These 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 [9, 10]. Over the last 60 years more than 30,000 different substances have been evaluated for their plasticizing properties. At present, about 100 different plasticizers are produced worldwide, although only about 50 of these are classified as commercially important. According to 2014 data, the total global market for plasticizers was 8.4 million metric tonnes including 1.3 million metric tonnes in Europe [11, 12].

This paper represents the influence of two modificators, namely plasticizer and bioplasticizer on the properties of PLA fibres and also the influence of degree of uniaxial deformation on the supermolecular structure and basic mechanical properties of modified PLA fibres. The undrawn and drawn modified PLA fibres by discontinuous technological process were prepared. The obtained experimental results were compared with unmodified PLA fibre prepared under the same technological conditions.

2 EXPERIMENTAL AND METHODS

2.1 Materials

Polylactic acid produced by NatureWorks LLC (PLA) with MFI=27.7 g/10 min (210°C/2.16 kg) and two modifiers: 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 Fibre preparation

The modified PLA/PL fibres were prepared from mechanical mixing blend of PLA granulated polymer and plasticizer using the classical discontinuous process of spinning and drawing. The same process for preparation of PLA/BioPL fibres was used.

The constant processing conditions for preparation of both types modified PLA fibres were following: spinning temperature of 210°C, spinning die plate of 2x25 holes with diameter of 0.3 mm, final spinning process speed of 1500 $m.min^{-1}$, the drawing temperature of 80°C and final drawing process speed of 100 $m.min^{-1}$. The different drawing ratios (DR) DR = 1.2, 1.4, 1.6 and DR_{max} for modified PLA fibres were used.

2.3 Methods used

The fibre´s birefringence (Δn): The orientation of the segments of macromolecular chains in fibre expresses the level of anisotropy of oriented polymer system (fibre). The total orientation of prepared modified PLA fibres was evaluated using polarization microscope DNP 714BI. The refractive indexes of light in the fibre axis ($n_{//}$) and in the perpendicular direction of fibre ($n_{\perp}$) were determined. From the difference of refractive indexes of light, the fibre birefringence was calculated.

Crystallinity of fibres β represents the crystalline portion of fibre which may be evaluated using various methods. In this work DSC-Q20 apparatus TA Instruments was used for the evaluation of thermal properties of unmodified and modified PLA fibres. The non-isothermal process of analysis was performed. All samples of PLA fibres were heated by rate of 10°C.min^{-1} from 60 to 200°C under nitrogen flow. From melting endotherm of 1st heating of PLA fibres the melting enthalpy (ΔH_m) was determined. The crystallinity β of PLA fibres was calculated according to the following equation 1 [13]:

$$\beta = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_{m,0}} \cdot 100\% \quad (1)$$

where: ΔH_{cc} is the cold crystallization enthalpy of PLA fibres obtained during heating scan and $\Delta H_{m,0}$ is the melting enthalpy of a 100% crystalline PLA (93.6 $kJ.kg^{-1}$) [14].

Mechanical properties of unmodified and modified PLA fibres were measured using Instron 3345 equipment in accordance with the EN ISO 2062 and fineness was measured in accordance with the EN ISO 2060.

3 RESULTS AND DISCUSSION

In the preparation of PLA fibres, it was found that the modifiers PL and BioPL do not affect the spinning process. The spinning of all samples was technologically stable in the whole evaluated range of 1-5 wt.% of modifiers and was comparable with the preparation of the PLA standard fibre without modifiers.

By a discontinuous unidirectional deformation procedure, the modified fibres together with the standard fibre were drawn to drawing ratios of 1.2, 1.4, 1.6 and DR_{max}. The effect of plasticizer (PL) content on fibre drawing did not appear. PLA/PL fibres were drawn to the same maximum drawing ratio as the standard fibre at all plasticizer concentrations of 1-5 wt.%, DR_{max} 1.8. The effect of the bioplasticizer (BioPL) on the process of unidirectional deformation of PLA/BioPL fibres was manifested at higher concentrations of BioPL - 4 wt.% and 5 wt.%, at which the fibres were drawn to DR_{max} 1.82.

The measured structural parameters of undrawn and drawn PLA/PL and PLA/BioPL fibres are given in Table 1. The mechanical properties (tenacity and elongation) of undrawn modified fibres are given in Table 2 and drawn fibres are put into Figures 1-3. The changes in properties of modified PLA fibres are compared to the standard fibre of the respective sample series (fibres with 0% modifier).

3.1 Structure properties

At higher contents of PL in PLA polymer matrix 3-5 wt.%, the total orientation of the segments of macromolecular chains (birefringence) of undrawn fibres increased by 16-24% compared to the standard undrawn fibre (Table 1, columns for PLA/PL fibres). This is due to the plasticizing effect of the modifier, which facilitates the straightening of the segments of the macromolecular chains of the PLA polymer melt during fibre spinning. The crystallinity of the undrawn PLA/PL fibres is practically unchanged, which may be due to the amorphous nature of the plasticizer. Similarly, in undrawn PLA/BioPL fibres, the total orientation of the segments of macromolecular chains increased by 10-18% with BioPL content above 3 wt.%, while crystallinity did not change significantly even with this type of modifier (Table 1, columns for PLA/BioPL fibres).

Unidirectional deformation (drawing) causes the macromolecular chains and their segments to be straightened in the direction of the fibre axis, thus creating a fibrillar structure. This results in an increase in the structural parameters of birefringence and crystallinity. A significant increase in the orientation of the segments of macromolecular chains occurs already at the lowest drawing ratio DR 1.2, where the increase of birefringence of PLA fibres is about 100% compared to undrawn fibres DR 1.0 (Table 1).

Due to PL, there is a further increase in the orientation of the segments of macromolecular chains of the drawn fibres compared to the standard fibre even at the lowest PL content of 1 wt.% at all drawing ratios. The most significant increase in birefringence was recorded at contents of 3 and 4 wt.% of PL and on the other hand the higher contents of PL - 4 and 5 wt.% slightly reduced the crystallinity of the fibres (Table 1, columns for PLA/PL fibres).

Table 1 Supermolecular structure parameters of PLA fibres modified by PL and BioPL

Modifier content [%]	Drawing ratio (DR)	PLA/PL fibres			PLA/BioPL fibres		
		$\Delta n.10^3$	$CV_{\Delta n}$ [%]	β [%]	$\Delta n.10^3$	$CV_{\Delta n}$ [%]	β [%]
0	1.0	6.11	1.34	0.323	6.62	1.32	0.308
0	1.2	10.54	1.94	0.343	12.71	2.41	0.330
0	1.4	16.67	2.29	0.355	15.32	2.12	0.349
0	1.6	19.41	1.49	0.364	19.91	2.84	0.354
0	max	22.81	1.32	0.381	21.78	2.55	0.372
1	1.0	6.34	2.03	0.326	7.18	2.27	0.313
1	1.2	14.85	2.28	0.347	13.94	3.05	0.351
1	1.4	18.15	2.73	0.350	19.45	3.10	0.358
1	1.6	21.55	2.11	0.354	20.71	2.28	0.362
1	max	23.57	1.71	0.383	22.66	2.84	0.394
2	1.0	6.21	2.14	0.327	6.53	3.08	0.322
2	1.2	16.53	2.81	0.350	12.59	3.12	0.347
2	1.4	18.63	1.15	0.356	17.63	2.75	0.356
2	1.6	21.35	1.31	0.370	20.87	2.91	0.364
2	max	22.67	1.63	0.387	23.79	3.15	0.396
3	1.0	7.59	2.86	0.336	7.82	3.14	0.320
3	1.2	10.34	2.41	0.345	14.74	3.55	0.347
3	1.4	18.85	2.23	0.357	18.77	3.08	0.356
3	1.6	22.21	1.85	0.369	21.87	2.64	0.371
3	max	23.01	1.53	0.389	23.14	2.77	0.404
4	1.0	7.29	2.20	0.333	7.28	3.33	0.312
4	1.2	16.67	2.82	0.340	13.83	3.17	0.344
4	1.4	21.42	2.64	0.353	18.07	3.09	0.363
4	1.6	23.17	2.32	0.362	21.04	2.87	0.370
4	max	24.11	1.44	0.378	24.21	2.99	0.415
5	1.0	7.09	2.71	0.321	7.76	3.17	0.338
5	1,2	15.95	1.19	0.335	16.65	2.77	0.355
5	1,4	18.17	2.25	0.351	19.02	2.84	0.373
5	1,6	21.03	2.63	0.359	22.57	3.27	0.380
5	max	23.08	2.44	0.376	24.55	3.19	0.422

Table 2 Mechanical properties (tenacity and elongation) of undrawn PLA/PL and PLA/BioPL fibres

Modifier content [%]	PLA/PL fibres				PLA/BioPL fibres			
	Tenacity [cN/dtex]	CV_T [%]	Elongation [%]	CV_E [%]	Tenacity [cN/dtex]	CV_T [%]	Elongation [%]	CV_E [%]
0	1.07	5.4	121.0	5.9	1.03	2.8	136.7	3.9
1	1.09	5.4	136.0	6.5	1.00	5.8	121.3	5.1
2	1.08	4.3	124.3	5.6	1.04	7.5	115.9	5.2
3	1.13	5.1	112.6	3.2	1.03	3.8	116.7	9.9
4	1.14	5.4	109.1	5.5	1.14	8.0	112.9	5.9
5	1.05	5.0	116.1	7.9	1.21	4.9	104.5	5.5

Higher content of BioPL above 3 wt.% caused a significant increase in the orientation of the segments of macromolecular chains of drawn fibres by an average of 15% (Table 1, columns for PLA/BioPL fibres).

The crystallinity of the PLA/BioPL fibres with content of bioplasticizer 4 wt.% and 5 wt.% in fibres, increased by 13% compared to the standard fibre at the maximum drawing ratio (DR_{max}). It is partly due to the higher DR_{max} achieved with the stated BioPL contents.

The slight increase in crystallinity of the drawn PLA/BioPL fibres compared to the standard fibre may be due to the content of the crystalline component of the bioplasticizer, which acts as a nucleating agent.

3.2 Mechanical properties

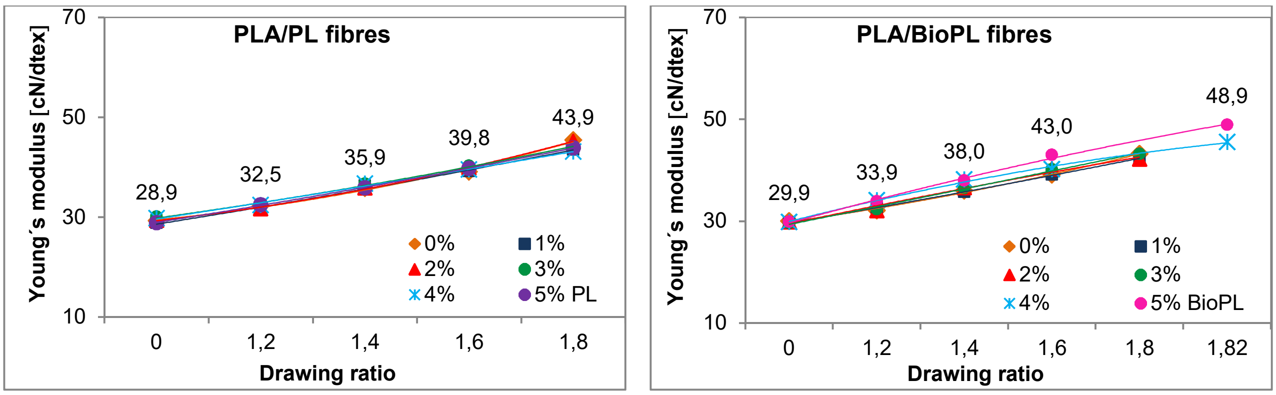
From the mechanical properties of undrawn PLA/PL fibres was found that, the effect of the plasticizer was not more pronounced in any of the evaluated mechanical properties (Table 2). For undrawn modified PLA/BioPL fibres, at higher bioplasticizer contents of 4 wt.% and 5 wt.% in the PLA polymer matrix, the tenacity was increased by 10-17% while reducing elongation by 24-32% absolute compared to the undrawn standard PLA fibre (Table 2).Young's modulus of elasticity was practically unchanged by the addition of the BioPL (Figure 1). Unidirectional deformation (drawing) leads to an increase in Young's modulus (Figure 1) and tenacity (Figure 2) which corresponds to the structural properties of the fibre (Table 1). Reciprocally, the elongation of the fibres decreases with the drawing ratio (Figure 3).

The tenacity of the drawn modified PLA/PL fibres was practically unchanged compared to the drawn unmodified PLA fibres at the same drawing ratios, which is probably related to the amorphous character of the plasticizer as already mentioned in the evaluation of the fibre structure. The highest tenacity of 2.24 and 2.25 cN/dtex was achieved for PLA/PL fibres containing 2 wt.% and 5 wt.% PL at their DR_{max}. Due to PL, the elongation decreases compared to the standard fibre at all drawing ratios up to a maximum of 28% absolute (Figure 3a). Young's modulus of elasticity of drawn modified PLA/PL fibres practically does not change with increasing plasticizer content (Figure 1a).

Unlike the plasticizer, the bioplasticizer positively affected the tenacity of PLA fibres. The tenacity of the drawn PLA/BioPL fibres was significantly increased by the influence of BioPL, at its content of 4 wt.% and 5 wt.% up to 50% compared to the standard fibres at the same drawing ratio (Figure 2b).

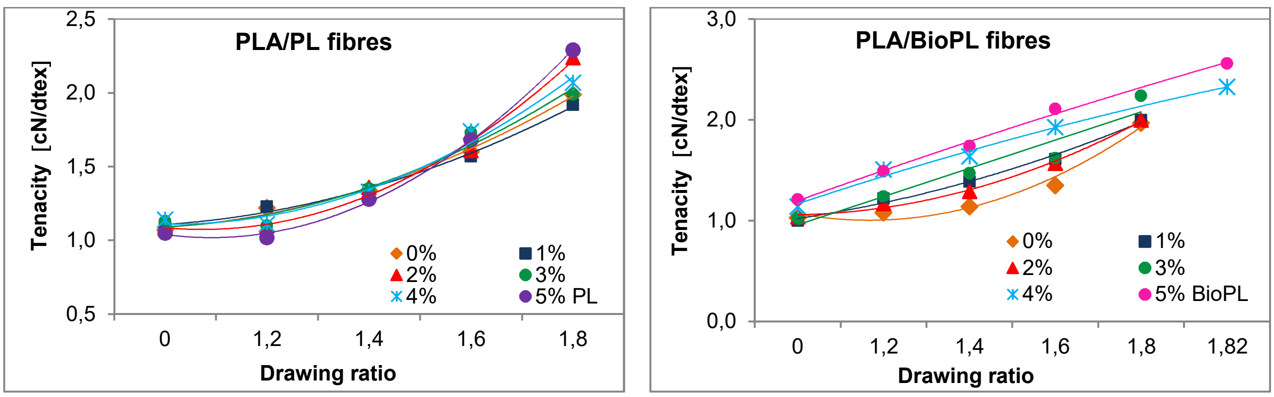
We can even state that with increasing BioPL content above 1 wt.%, the tenacity of the fibres also increases. This is probably due in part to the crystalline nature of the bioplasticizer, where the higher the bioplasticizer content, the more nucleation centers are formed, which has a positive effect on increasing the tenacity. The highest tenacity of 2.56 cN/dtex was achieved with a fibre containing 5 wt.% BioPL at its DR_{max} (Figure 2b).

With an increase in tenacity, there is a slight decrease in elongation up to max. 17% absolute compared to PLA standard fibres at the same drawing ratio. The Young's modulus of elasticity of the drawn modified PLA/BioPL fibres increased at 5 wt.% bioPL at DR_{max} by 13%, due to the effect of a higher drawing ratio compared to the standard fibre at DR_{max}. In other cases, the Young´s modulus of elasticity practically unchanged under the influence of the BioPL modifier (Figure 1).



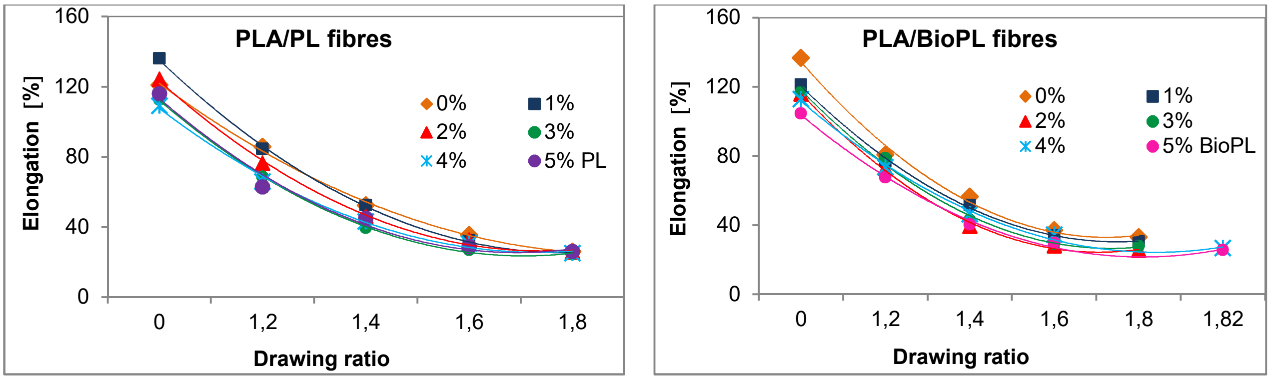
a) b)

Figure 1 The dependence of Young's modulus of PLA fibres on drawing ratio: a) fibres with the content of plasticizer (PL) and b) fibres with the content of bioplasticizer (BioPL) together with standard fibre; content of modifier is 1-5 wt.% in fibre. The values shown in the Figure 1 correspond to fibers containing 5 wt.% of modifier



a) b)

Figure 2 The dependence of tenacity of PLA fibres on drawing ratio: a) fibres with the content of plasticizer (PL) and b) fibres with the content of bioplasticizer (BioPL) together with standard fibre; content of modifier is 1-5 wt.% in fibre



a) b)

Figure 3 The dependence of elongation PLA fibres on drawing ratio: a) fibres with the content of plasticizer (PL) and b) fibres with the content of bioplasticizer (BioPL) together with standard fibre; content of modifier is 1-5 wt.% in fibre

4 CONCLUSION

The preparation of PLA fibres containing modifiers PL and BioPL was performed under the same conditions as the preparation of standard fibres. It was found that the addition of modifiers of 1-5 wt.% to the PLA polymer matrix did not affect the spinning process. Plasticizer PL also did not affect the discontinuous drawing process, modified PLA/PL fibres were drawn to the same drawing ratios as the standard fibre 1.2, 1.4, 1.6 and DR_{max}. PLA/BioPL fibres achieved a higher DR_{max} 1.82 at 4 wt.% and 5 wt.% of bioplasticizer.

The evaluation of the structural and mechanical properties of modified PLA fibres shows that the bioplasticizer has a more significant effect on the change of structural and mechanical properties compared to the plasticizer. This is probably due to their different nature, the plasticizer has an amorphous character and the bioplasticizer contains a small part of crystalline component. BioPL increases birefringence, slightly increases crystallinity in the fibres, and significantly increases tenacity while decreasing elongation. PL significantly increases the birefringence PLA fibres and slightly reduces the elongation of the fibres. PL has no significant effect on the tenacity. Young's modulus was practically unchanged by both modifiers.

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